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The reaction of iron (II) with the vic-dioximes in the presence of amines

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THE REACTION OF IRON(II) WITH THE VIC-DIOXIMES IN THE PRESENCE OF AMINES

by

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I. INTRODUCTION

In 1905 Tschugaeff discovered and studied the reaction between 2,3-butanedionedioxime and Ni(II). In this same work he also reported that when 2,3-butanedionedioxime was reacted with Fe(II), a red-violet color was produced. It was stated that this was a very sensitive test for the presence of iron. In subsequent research it was also determined that the red-violet color was only produced when a primary amine or ammonia was present. As a final bit of information, Tschugaeff reported that he had succeeded in crystallizing out some of the complex. The analysis of the crystals led to the formula $Fe(DH_2)_2(A)_2$, where DH_2 represents the vic-dioxime molecule and A represents an amine molecule.

To the present, very little more has been added to the information Tschugaeff advanced over one half century ago. The reaction has occasionally been used as an analytical method down through the years. As recently as 1954 Oi reported its use in a colorimetric iron determination.

There were three objectives of the research described herein. The first was to determine the nature of the reaction or reactions involved in the formation of the red-violet iron-vic-dioxime-amine complex or complexes. The second was to study the properties of a newly synthesized and unstudied vic-dioxime as applied to the determination of iron. The third was to generally evaluate the reaction as

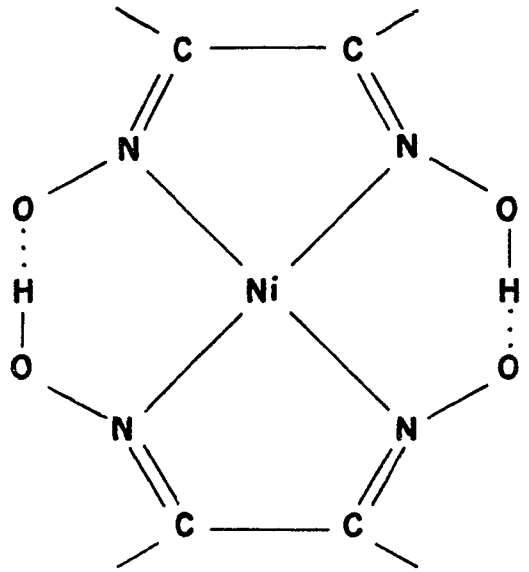
a colorimetric method for iron and if it was found to be suitable, to recommend the optimum conditions for its use.

II. REVIEW OF LITERATURE

A. The Chemistry of the vic-Dioximes

The application of 2,3-butanedionedioxime to the determination of nickel and palladium has been known for over fifty years. 2,3-butanedionedioxime is commonly referred to as dimethylglyoxime and will henceforth be identified by this name. Most of the basic information available about the chemistry of the vic-dioximes has only been advanced in recent years. In addition, practical syntheses of vic-dioximes other than dimethylglyoxime have recently broadened the scope of the field greatly.

Three isomeric forms of the vic-dioximes are known, the α-(anti-), β-(syn-), and γ-(amphi-) forms. Of the three, only the α-form has been of any analytical importance. Feigl and Suter (11) have shown that a vic-dioxime can act in any one of three distinct ways: as a neutral compound, DH_2; as a monobasic acid, DH^-; as a dibasic acid, $D^=$. In the classic reaction with Ni(II) the vic-dioximes react as monobasic acids. A Ni(II) ion replaces one hydrogen ion from each of two vic-dioxime molecules to form the complex $Ni(DH)_2$. The following structure illustrates the generally accepted planar form of the molecule:



Recent work by Godycki (13) has indicated that an unusually stable hydrogen bond is present in this molecule. Palladium is precipitated by the vic-dioximes in dilute mineral acid solution and the structure of the compound formed is thought to be analogous to that of the Ni(II) precipitate.

Although the vic-dioximes are generally thought to be selective, some interferences are encountered. Bismuth gives a yellow colored precipitate or solution with dimethylglyoxime in hot, concentrated, ammoniacal solution. In slightly alkaline solution Cu(II) forms a violet color with dimethylglyoxime. Cobalt gives a brown color with dimethylglyoxime in the presence of ammonia. Iron(II) interferes by forming a yellow-brown solution or precipitate. The nature of this interference was studied by Byrd (5) and shown to be due to the complex $Fe(DH)_2 \cdot 2H_2O$. When ammonia or an amine is present

the interference takes a different form. A brilliant red-violet color is observed which is easily mistaken for a trace of nickel.

In recent years several other vic-dioximes have become widely used as reagents for nickel. Among these are two which are perhaps better known than any others. In 1924 Wallach (42) reported that 1,2-cyclohexanedionedioxime was water soluble and acted as a very sensitive reagent for nickel. The common name nioxime has been given to 1,2-cyclohexanedionedioxime, and this name will be used in referring to this compound. Little use was made of this compound until Rauh, Smith, Banks, and Diehl (27) succeeded in synthesizing it at moderate cost. As the analytical applications of nioxime were studied, it became apparent that the interference of Fe(II) was again a serious problem. In the case of dimethylglyoxime the iron interference could be masked with citrate or tartrate. Nioxime, however, forms a more stable complex with iron since neither citrate nor tartrate could eliminate the interference (39).

A practical synthesis for 1,2-cycloheptanedionedioxime was described by Vander Haar, Voter, and Banks (36) in 1949. The common name heptoxime has been given to 1,2-cycloheptanedionedioxime, and this name will be used in referring to this compound. Heptoxime forms a yellow precipitate with nickel as opposed to the normally encountered red. The

expected interference from Fe(II) in this case can be eliminated by citrate or tartrate.

B. The Iron(II)-*vic*-Dioxime-Amine Complexes

The first research dealing with the analytical applications of the *vic*-dioximes was done by Tschugaeff (32, 33). He reported that the interference of Fe(III) was a serious problem in the nickel determination. Ferric hydroxide was precipitated under the conditions employed. One of the methods used to eliminate this interference was reduction of the Fe(III), since Fe(II) hydroxide precipitates at a considerably higher pH. When this was done an intensely colored purple solution was encountered. The source of this color was shown to be the formation of a complex involving Fe(II), dimethylgloxime, and an amine. Tschugaeff succeeded in preparing well defined crystalline products by reacting *vic*-dioximes with nickel, platinum, palladium, cobalt, and copper. In the case of iron, considerable difficulty was experienced in preparing a solid derivative. One form was finally isolated, however, consisting of two moles of 2,3-pentanedionedioxime and two moles of pyridine for each ferrous ion.

In 1914 Tschugaeff and Orelkin (34) investigated this reaction further and reported that the purple color was produced only in the presence of ammonia or an amine. The

authors also pointed out that the reaction could be used as a qualitative test for iron sensitive to one part in 20,000,000. In addition, they also reported that the reaction was suitable for the quantitative colorimetric determination of small amounts of iron.

In the years since the original work, very little additional information has been presented with the exception of several papers published in the last decade. Slawik (29) studied the qualitative aspects of the reaction in 1912. Vaubel (37) first noted that in the absence of any amine, a yellow color was obtained by reacting Fe(II) with dimethylglyoxime. Kraus (19) discussed the ease of confusing the red color of this reaction with that due to nickel. None of these workers contributed anything of importance to the theory or general usage of this method of iron determination.

Prill and Hammer (26) reported in 1937 the use of this reaction in the determination of dimethylglyoxime by the addition of an excess of Fe(II) ion. Charlot (7) reported that the Fe(II)-dimethylglyoxime complex served as an oxidation-reduction indicator. Matthews (23) expanded on this work using nioxime and reported the same effects as Charlot. A color change from red to yellow is observed. The yellow color was undoubtedly that which was observed by Vaubel (37) when he reacted dimethylglyoxime with Fe(III). Matthews estimated that the reduction potential of the nioxime complex

was -0.6 volts which is so low that it is out of the range usually employed in oxidation-reduction titrations.

Diehl (8) pointed out that further work on this reaction seemed desirable and presented a short historical review in 1940.

Griffing and Mellon (15) conducted the first contemporary study of the reaction utilizing modern techniques in 1947. Their work was directed toward an evaluation of the reaction as a colorimetric method for iron. One major contribution made was the discovery that the color could be stabilized by the addition of sodium dithionite, $Na_2S_2O_4$, which is a strong reducing agent in basic solution. They studied four vic-dioximes: diethylaminobutanedionedioxime, diphenylethanedionedioxime, di(2-furyl) ethanedionedioxime, and nioxime. The amines used were isobutylamine, sec-butylamine, n-butylamine, isoamylamine, n-amylamine, and pyridine. The factors studied were: reducing agents, amine concentration, reductant concentration, vic-dioxime concentration, order of addition of reagents, iron concentration, stability of the system, and the effects of diverse ions. In each case only the conditions yielding satisfactory results were given. No mention was made of the effects of pH on the systems involved. This paper like its predecessors made no attempt to elucidate the nature of the complex or complexes formed.

Matthews and Diehl (24) made a more exhaustive study of the reaction of Fe(II) with nioxime. They established by the method of continuous variations (18, 38) that the ratio of nioxime to iron was two to one when ammonia was serving as the amine in the reaction. No statement was made as to the time between the formation of the complex and determination of the absorbance. As will be shown subsequently, this point can be somewhat critical. Perhaps the most significant contribution of this work were the ion migration studies using the iron-nioxime complexes with ammonia and ethylenediamine. In both of these cases the color was observed to migrate toward the anode of a simple electrolytic cell, indicating that the colored species was an anion. This finding is especially significant when considered in the light of the work of Feigl and Suter (11).

Feigl and Suter (11) demonstrated that it is quite possible for a vic-dioxime to act as a dibasic acid. By working in strongly basic solution they were able to convert the normally encountered palladium-dimethylglyoxime precipitate, $Pd(HD)_2$, into $K_2Pd(D)_2$. A series of similar compounds were prepared by substituting different ions for potassium. This work indicated without a doubt that a vic-dioxime can be doubly ionized in a basic solution. In the same paper the authors postulated that the iron-vic-dioxime complexes were of the same nature; i.e., $(NH_4)_2Fe(D)_2$.

Byrd (5) has shown in an acetate buffered solution in the absence of amines that the ratio of nioxime to iron is two to one by the method of continuous variations and by analysis of the solid formed. The analysis of the solid compound gave results which corresponded to the formula $Fe(HD)_2 \cdot 2H_2O$.

C. The Aqueous Chemistry of Iron

Iron is a much studied and extremely well characterized element. In aqueous solution two oxidation states are most commonly encountered - Fe(II) and Fe(III). Iron(III) is generally considered more stable than Fe(II) in solution. Iron(II) is oxidized by the air to Fe(III) at varying rates depending on the pH of the solution involved. At a pH above 3 the oxidation proceeds quite readily due to the hydrolysis of Fe(III) and the extreme insolubility of Fe(III) hydroxide. Iron(II) can be satisfactorily maintained in solution by excluding air and other oxidizing agents from the solution. It can also be stabilized by the addition of a strong reducing agent.

The complexes of both Fe(II) and Fe(III) are many and varied. A large number are colored and have been applied to colorimetric methods. Both organic and inorganic anions are known to complex iron with varying degrees of tenacity. In general these complexes are octahedral since both Fe(II) and

Fe(III) have an electronic configuration capable of the d^2sp^3 structure. There are also reports that both ions form tetrahedral complexes (21) and there is some evidence that Fe(II) may form square planar complexes in isolated cases (25).

There are other forms of iron found in aqueous solution such as $FeO_3^=$ and $FeO_4^=$. These are ordinarily found only in strongly alkaline solution and have no bearing on the problem at hand.

D. Methods for Determining Stability Constants of Metal Chelates

1. Potentiometric (pH)

The determination of complex stability constants by means of pH measurement is undoubtedly one of the best techniques available. In many cases it is the most accurate and reliable method. Theoretically, any chelate which is water soluble may be studied by this method. The pH of a solution is always affected by the formation of a chelate since all chelating agents are either acids or bases and the formation of a chelate with a metal ion involves the liberation of a proton from an acid or a decrease in the concentration of a base. These effects should be detectable with an appropriate instrument. The stability constant or constants should then be calculable from the pH effects observed. Generally a

titration procedure is employed but this is not always the case. There are a considerable number of calculation techniques known (21) but these will not be given here since this technique was not found to be effective in the buffered system used in this research.

2. Polarographic

There are two general methods of utilizing polarographic measurements in the determination of the stability constants of metal chelates. The first, described by Lingane (20), is based on the shift in the reduction potential of a metal at the dropping mercury electrode to a more negative value when the metal is present in the form of a complex. Under certain conditions concentration and potential measurements may be used to calculate the stability constant and formula of a complex.

The second technique, utilized by Wheelwright, Spedding, and Schwarzenbach (44), is based on the use of the polarograph to determine the equilibrium concentration of a free metal ion. In this method the complex is formed and allowed to come to equilibrium under the desired conditions. The free metal ion concentration is then measured and from this and the known total concentrations the stability constant can be calculated. This technique may be modified by allowing two metal ions to compete for the same chelating agent.

A solution of the complex of one metal is mixed with a solution of a salt of the metal under study. After equilibrium is attained the new concentration of the originally complexed metal is determined polarographically. The stability constant of the second metal with the chelating agent can then be calculated if the stability constant of the first complex is known.

3. Spectrophotometric

The terminology of spectrophotometry recommended by Hughes (17) has been followed.

A = Absorbance = $\log_{10}(1/T)$

ϵ = Molar Absorptivity (Molar Absorbancy Index or Molar Extinction Coefficient)

b = Internal cell length in centimeters

There are a number (21) of methods of determining the formula and stability constants of metal chelates by a study of optical properties. Most methods for stability constant determination assume that the formula is already known. If the formula is not known these methods cannot be used. The means of circumventing this problem are the method of continuous variations (18, 38) and the slope-ratio method of Harvey and Manning (16).

The method of continuous variations is based on the variance observed in the absorbance of a series of solutions

in which the total mole fraction of the two variable constituents is kept fixed. The plot of variance in absorbancy against the mole fraction of one of the variable constituents results in two straight lines which intersect at a point. The ratio of one constituent to that of the other which produces the maximum absorbance, hence the maximum amount of complex formed, is determined from this plot. From this ratio the complex formula is easily found.

In the slope ratio method the general reaction

$$mD + nB = D_mB_n$$

is used. If the concentration of B is held in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex will be essentially proportional to the analytical concentration of D in the reaction, so

$$[D_mB_n] = C_D/m$$

where the brackets refer to equilibrium concentration and C to the analytical concentration.

From Beer's law there is the relation

$$A = \epsilon\, b\, [D_mB_n] \quad .$$

Substituting the first equation into the second

$$A = \epsilon\, bC_D/m$$

A is plotted against different analytical concentrations of D, keeping the concentration of B constant and in excess. Over the straight line portion of the curve, the slope is represented by

$$\text{slope}_1 = \epsilon\, b/m$$

Similarly if D is the component in constant excess and the concentration of B is varied

$$[D_m B_n] = C_B/n$$

and if D is plotted against C_B, the slope of the straight line portion of the curve will be

$$\text{slope}_2 = \epsilon\, b/n$$

The ratio of n to m in the complex may be determined by taking the ratio of the two slopes

$$\frac{\text{slope}_1}{\text{slope}_2} = \frac{n}{m}$$

This method serves to establish the ratio of color forming radical to the metal ion.

The evaluation of the stability constant once the formula of the complex is established can be done in several ways; two of which will be elucidated here.

In the simple equilibrium (21)

$$M + Ke = MKe$$

in which only the chelate MKe absorbs in the wavelength being studied we may write

$$K = \frac{[MKe]}{[M][Ke]} \quad .$$

If A is the absorbance of a solution and Beer's law holds, it follows that

$$[MKe] = kA$$

where k is the proportionality constant.

For two solutions yielding equal absorbance readings but having different concentrations of metal and chelating agent,

$$[MKe]_1 = kA_1 \qquad [MKe]_2 = kA_2$$

$$A_1 = A_2 \qquad [MKe]_1 = [MKe]_2 = [MKe]$$

We may then write:

$$K = \frac{[MKe]}{(Cm_1 - [MKe])(C_{Ke_1} - [MKe])} = \frac{[MKe]}{(Cm_2 - [MKe])(C_{Ke_2} - [MKe])}$$

where Cm_1 and Cm_2 are the total concentrations of free and combined metal species in solutions 1 and 2. C_{Ke_1} and C_{Ke_2} are the total concentrations of free and combined chelating

agent species in solutions 1 and 2. Since these four latter values are known the above equations may be solved for [MKe] and K.

A second method (35) of determining the stability constant is based on the measurement of the absorbance of the chelate when one of the substituents is present in great excess. Under these conditions the formation of the chelate may be considered complete. Since this is necessary it is important that the reagent in excess have not even a weak absorption band at the wavelength used. Under these conditions the molar absorptivity may be calculated by applying Beer's law. Measurements of the absorbance are then made at concentrations of the reagents such that the formation of the chelate is not complete and the concentration of the chelate must be calculated by means of Beer's law. If the formula of the chelate is known, the concentration of the free metal ion and of the chelating agent may be determined and the constant calculated.

A technique developed by Diehl and Sealock (9) is capable of determining both the combing ratio and the stability constant simultaneously. For the reaction

$$M + nD' = MD_n$$

where D' represents all the various ionic species of D that are not involved in the chelate, the formation constant may

be expressed as:

$$K = \frac{[MD_n]}{[M]\,[D']^n}$$

Converting this equation to logarithmic form we obtain,

$$\log K = \log \frac{[MD_n]}{[M]\,[D']^n}$$

This equation can be rearranged to correspond to the equation of a straight line.

$$\log \frac{[MD_n]}{[M]} = n \log [D'] + \log K$$

Plotting $\log [D']$ versus $\log \frac{[MD_n]}{[M]}$, the slope is equal to 'n' and the y intercept is log K.

There are a number of ways of applying this method and the exact way it was used in the present work will be described in a later section. It should be mentioned that the method as described above yields not thermodynamic equilibrium constants, but 'apparent' formation constants which are only valid for systems in which the conditions, especially pH, are similar or the same as those used to determine the constant.

4. Other methods

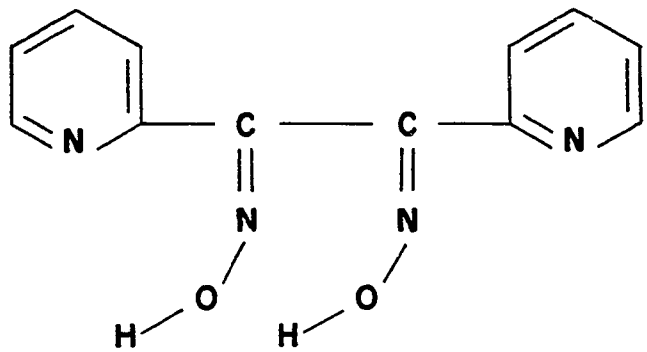
There are, of course, a large number of other techniques for determining stability constants which will not be discussed

in detail. These are generally applicable to very few systems and are not regularly encountered. Methods involving ion exchange, reduction potential determination, solubility and conductivity measurements, precipitation and extraction, and reaction rates were considered but disregarded since they were not suitable to the systems under study.

III. PREPARATION STUDIES

A. Preparation of 2,2'-Pyridildioxime

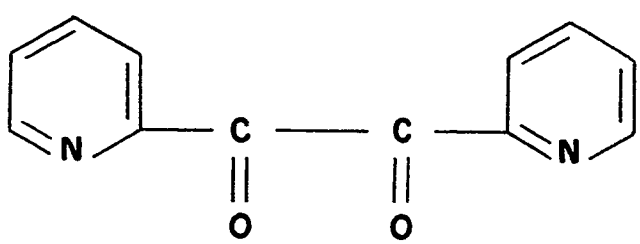
This compound was first reported by Mathes, Sauermilch, and Klein (22) in 1951.



Their work dealt primarily with the preparation of the parent diketone, 2,2'-pyridil, and related compounds. 2,2'-pyridildioxime was prepared as a confirmatory derivative of the parent diketone. The authors stated that the dioxime melted at 215°C and yielded a cherry red color when reacted with ferrous sulfate.

1. Preparation from 2,2'-pyridil

A sample of 2,2'-pyridil was obtained from F. Raschig of Ludwigshafen, Germany.



The material as received was a light orange color. Recrystallization from ethanol yielded light yellow crystals with a melting point of 154-155°C. Further recrystallization failed to make any noticeable change in the color or melting point, so the material was assumed to be fairly pure.

The presence of any dioxime in any particular reaction mixture was easily confirmed. A small portion of the reaction mixture was pipetted into a dilute solution of ferrous sulfate. The characteristic red color was a confirmatory test for the presence of the dioxime.

(a) Preparation in acidic media. Two different attempts to synthesize 2,2'-pyridildioxime in an acidic medium were made. The first was done in aqueous solution. Two g. of the diketone, 2,2'-pyridil, were mixed with five g. of hydroxylamine hydrochloride (Baker and Adamson, A.C.S. grade) in 100 ml. of water. Two ml. of hydrochloric acid were added and the mixture was stirred for nine hours at room temperature. Another experiment was set up similar to the first except that it was refluxed for nine hours. The test for the presence of the dioxime previously described was applied and yielded a positive test in both cases.

The second attempt was similar to the first except that it was carried out in ethanol. Two g. of the diketone were mixed with five g. hydroxylamine hydrochloride in 100 ml. of ethanol. Two ml. of hydrochloric acid were added and the

mixture stirred for nine hours at room temperature. As in the aqueous experiment a second run was made in which all conditions were the same except that the mixture was refluxed with stirring for nine hours. The test for the dioxime was applied and both reaction mixtures gave a positive test with ferrous iron.

In the work up of the reactions described above, the excess hydrochloric acid present was neutralized to precipitate the dioxime. In each case only a trace of the dioxime was isolated. A number of other attempts were made to isolate more product but the yields were apparently so low that this line of work was abandoned. Since the reaction was known to proceed well in basic solution no further attempts were made to use acidic conditions.

(b) Preparation in basic media. Three sets of conditions were tried. The first attempt was made using potassium hydroxide in ethanol. Two g. of 2,2'-pyridil, 3 g. of hydroxylamine hydrochloride, and 8 g. of potassium hydroxide were mixed with 100 ml. of ethanol and refluxed for five hours. The reaction mixture gave a positive test for the presence of the dioxime. At the end of the allotted time the mixture was placed in an air stream and evaporated to a thick, pink paste. This residue was then stirred with 200 ml. of water until dissolved. Small particles of dry ice were added to neutralize the excess potassium hydroxide. The resultant

precipitate was filtered off and dried in a vacuum oven at 60°C under a vacuum of 29 inches of Hg. The yield of crude product was 45 per cent.

The second attempt was made in ethanol using pyridine as the base. Two g. of 2,2'-pyridil, 3 g. of hydroxylamine hydrochloride, and 10 ml. of pyridine were mixed with 100 ml. of ethanol and refluxed with stirring for five hours. The reaction mixture gave a positive test for the presence of the dioxime at this time. As in the previous experiment, the mixture was evaporated to a pink paste and then dissolved in 100 ml. of water. The solution was neutralized with dry ice and the resultant precipitate filtered off and dried in a vacuum oven under a vacuum of 29 inches of Hg at 60°C. The yield of crude dioxime was 28 per cent.

The third attempt was made in aqueous solution using potassium hydroxide as the base. Two g. of 2,2'-pyridil and 3 g. of hydroxylamine hydrochloride were mixed with 30 ml. of water and cooled to 0°C. Fifteen grams of potassium hydroxide were dissolved in 70 ml. of water and cooled to 0°C. The potassium hydroxide solution was then added dropwise with stirring to the mixture of diketone and hydroxylamine over the course of twenty minutes. This mixture was then refluxed with stirring for five hours. The reaction mixture gave a positive test for the presence of the dioxime. Dry ice was added to neutralize the solution to a pH of 7 and the result-

ant precipitate filtered off and dried in the vacuum oven at 55°C and 29 inches of Hg. The yield of crude product was 73 per cent.

Since the yield of the latter reaction was much greater than the two run in ethanol, all further work was done in aqueous solution. To study the time and temperature requirements of the reaction the following general procedure was used: 5 g. of 2,2'-pyridil (0.0206 moles) and 10 g. of hydroxylamine hydrochloride (0.142 moles) were mixed with 30 ml. of water and cooled to 0°C. Fifteen grams of potassium hydroxide (0.268 moles) were dissolved in 120 ml. of water and cooled to 0°C. The potassium hydroxide solution was added dropwise with stirring to the mixture of the diketone and hydroxylamine. The mixture was then heated to the desired temperature and held there for the desired length of time. Dry ice was then added to neutralize the excess potassium hydroxide to a pH of 7 and the resultant precipitate filtered off and dried in the vacuum oven. The filtrate was saturated with potassium nitrate and the resultant precipitate washed with water and combined with the other precipitate.

The series of experiments to determine the temperature effect showed that it is desirable to run the reaction almost at the boiling point of water. Each reaction was run for four hours. The yields of the reactions run at 97°C, 90°C, 80°C, and 60°C were 89 per cent, 72 per cent, 51 per cent,

and 26 per cent, respectively. All subsequent reactions were run on a steam plate at temperatures between 95°C and 98°C.

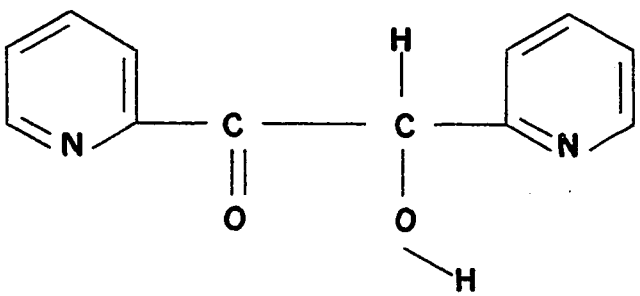
The series of experiments to determine the effect of reaction time showed that two hours is sufficient to produce a satisfactory yield. Each reaction was run between 95°C and 98°C on a steam plate. The yields from reactions run for 1, 2, 3, 4, and 5 hours were 69 per cent, 87 per cent, 89 per cent, 90 per cent, and 85 per cent, respectively. All subsequent reactions were run for two hours.

Conditions to produce larger quantities of the dioxime were studied. Seventy five g. of hydroxylamine hydrochloride (1.06 moles) and 25 g. of 2,2'-pyridil (0.103 moles) were mixed in 250 ml. of water. One hundred g. of potassium hydroxide (1.8 moles) were dissolved in 450 ml. of water and cooled to room temperature. The potassium hydroxide solution was added with stirring over a period of fifteen minutes. The mixture was then placed on a steam plate for two hours and stirred occasionally. After the allotted time the solution was clear and bright red in color. The red color was undoubtedly due to the formation of a complex with the traces of iron in the reagents. One half pound of dry ice broken into small particles was then added to reduce the pH to 7. The precipitate was filtered off and the filtrate saturated with potassium nitrate. The second batch of precipitate was filtered off and washed with a few small portions of water

to remove the entrained saturated potassium nitrate solution. The precipitates were combined and dried at 60°C under a vacuum of 29 inches of Hg. The average yield from a series of these reactions was 85 per cent. It was discovered in this work that the cooling of the reactants prior to mixing had little or no effect on the yield so the technique was abandoned. The final product was a light pink powder.

2. Preparation from 2,2'-pyridoin

A sample of 2,2'-pyridoin was also obtained from F. Raschig.

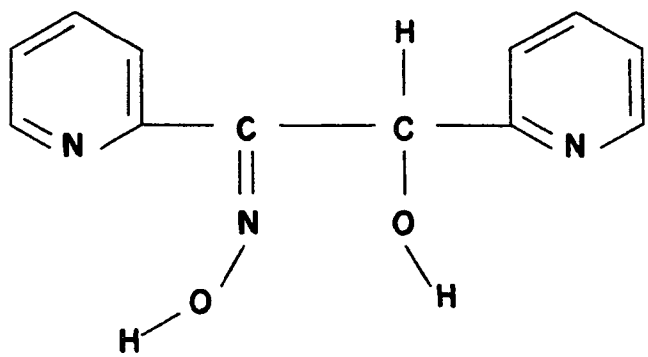


When this material was substituted for 2,2'-pyridil and subjected to the reaction conditions described previously for the preparation of 2,2'-pyridildioxime in basic solution, 2,2'-pyridildioxime was obtained. This phenomenon is attributed to a base catalyzed air oxidation of the alcohol group to a keto group and subsequent substitution of a hydroxylamine molecule to form the dioxime. The proof that the two products were identical was supplied by infrared

spectra. This phenomenon seems to indicate that the dioxime is quite stable thermodynamically.

B. Preparation of 2,2'-Pyridoinoxime

It was desired to produce a sample of 2,2'-pyridoinoxime in order to demonstrate that the iron complex of 2,2'-pyridildioxime was primarily formed by the two oxime groups.



As previously stated, it was not possible to synthesize this compound in basic solution. The material believed to be that desired was prepared in an acidic system from which all air had been excluded. This belief was substantiated by the infrared spectrum which exhibited peaks characteristic of oxime and alcohol groups. No complex with iron that yielded any color in the visible region of the spectrum was formed by this material.

The preparation required considerable care in order to prevent oxidation of the product. Five g. of 2,2'-pyridoin (0.023 moles) and 5 g. of hydroxylamine hydrochloride (0.071 moles) were mixed with 100 ml. of ethanol. Nitrogen was bubbled through the system throughout the entire course of the

reaction. Five ml. of hydrochloric acid were added from a dropping funnel and the mixture refluxed for three hours. The mixture was then neutralized with a 6 M potassium hydroxide solution which had previously been boiled. The white precipitate obtained was recovered and recrystallized from ethanol. A total nitrogen determination yielded a value of 19.3 per cent as compared with a theoretical value of 19.6 per cent.

C. Purification and Analysis of 2,2'-Pyridildioxime

The purification of the synthetic product proved to be somewhat of a problem. The impure material had a pink color which was assumed to be due to absorbed or adsorbed iron-hydroxylamine-dioxime complex. The crude product was found to be insoluble in the standard recrystallizing solvents such as dimethylformamide, trichloroethylene, dioxane, and benzene. It displayed an almost infinite solubility in pyridine and a very slight solubility in ethanol. After considerable study, a mixture of two volumes of pyridine to five volumes of absolute ethanol was found to be quite satisfactory. When hot (b.p. of ethanol), 100 ml. of this mixture dissolved up to five grams of the crude dioxime. When the solution was cooled with stirring, the pink color remained in solution while the dioxime crystallized out over a period of several hours. The filtered solid was pure white after several wash-

ings with cold ethanol. The product was dried in the vacuum oven at 60°C. It was found to decompose at 215°C in the same manner as the impure material. Further recrystallization effected no change in the decomposition point, infrared spectrum, or nitrogen analysis.

Great difficulty was encountered in attempting to determine the nitrogen content of the product by the Kjeldahl method. None of the various techniques tried gave results which were even close to the theoretical value. The method was abandoned in favor of the Dumas method. This worked well and indicated that the product was quite pure. Values averaging 22.9 per cent nitrogen were obtained as compared to the theoretical value of 23.1 per cent. Samples of the impure pink material were also analysed by this method and gave a nitrogen analysis of 22.8 per cent. A pure standard run at the same time also yielded results which were low by a comparable amount. The error was probably due to a calibration error in the nitrometer tube. The product was assumed to be at least 99 per cent pure.

One factor of interest in 2,2'-pyridildioxime is that the dioxime groups have a steric configuration which is not the same as the other well known vic-dioximes. It does not precipitate nickel at any pH. This fact indicates that the dioxime groups are in the syn- or amphi- form rather than the anti- form. 2,2'-pyridildioxime produces no visible re-

action with Fe(III), Ni(II), Al(III), Cd(II), Co(II), Mn(II), Hg(II), Ag(I), Sn(IV), Sn(II), Th(IV), or Zn(II) ions. It yields a light blue-green color with Cu(II) and a yellow color with Fe(II). This fact would seem to indicate that this dioxime would be a good reagent for iron. The obvious drawback is that one condition for maximum color development with Fe(II) is a pH value above 9.5. At this pH the metal ions listed above precipitate as hydroxides and thus interfere badly.

IV. DETERMINATION OF THE ACIDIC IONIZATION CONSTANTS OF 2,2'-PYRIDILDIOXIME

A. Materials and Apparatus

1. Water

Distilled, deionized water was used to make all solutions.

2. Potassium chloride

The potassium chloride used in this work to maintain the ionic strength of solutions at 0.1 was recrystallized from water and dried at 110°C overnight.

3. Potassium hydroxide solution

A solution which was approximately 6 M was prepared from Baker and Adamson reagent grade potassium hydroxide.

4. 2,2'-pyridildioxime solution

A 4×10^{-4} M solution of 2,2'-pyridildioxime was prepared by weight in a 0.1 M potassium chloride solution. The solution was made by mixing 0.0968 grams of 2,2'-pyridildioxime with approximately 900 ml. of 0.1 M potassium chloride solution. Since the dioxime was not readily soluble, the potassium hydroxide solution previously described was added dropwise until solution was complete. The pH was then adjusted

to 3 with hydrochloric acid and the solution was diluted to one liter with 0.1 M potassium chloride solution.

5. Spectrophotometer

A Beckman model DU was used to make all optical measurements in this section.

6. Measurement of pH

Throughout this study a Beckman model G pH meter was used. Used with this meter were a Beckman type E-2 shielded glass electrode (useful over the entire pH range) and a Beckman saturated calomel electrode. Both electrodes were for use external to the meter. The meter and electrodes were checked by standardization against the National Bureau of Standards buffers recommended by Bates (4). The buffer stock solutions were stored in polyethylene bottles from which small samples were taken and kept in a constant temperature bath maintained at 25°C for standardization.

B. Experimental Procedure

The acidic ionization constants of the vic-dioximes are an important factor in their ability to form chelates with metal ions. The formation of such a chelate involves the rupture of one or both of the hydrogen-oxygen bonds in the oxime groups and rebonding with a metal ion. The ease of

removal of the hydrogen ions is expressed by the acidic ionization constants.

The acidic ionization constants of the vic-dioximes are very small; hence, they cannot be determined by conventional titration techniques. Banks and Carlson (3) determined the ionization constants of dimethylglyoxime, nioxime, and heptoxime by employing the ultraviolet spectra of the various species involved. The ultraviolet spectrum of a non-ionized vic-dioxime molecule has an absorption peak near 225 millimicrons. The exact value varies slightly from one compound to another. The singly ionized species has an ultraviolet spectrum which exhibits a peak near 265 millimicrons. Again the exact value depends on the compound in question. The species present in any given system depends on the pH. By preparing a series of vic-dioxime solutions in which the pH was varied from 6 to 13, Banks and Carlson were able to evaluate the ionization constants by utilizing the known pH of the various solutions and the measured value of the absorbance at the wavelengths at which the peaks occurred. They employed two different methods of calculation. The first method was that of Stenstrom and Goldsmith (31) which was designed for determining the ionization constants of weak monobasic acids from spectrophotometric data. These workers have shown that the first molar ionization constant, K_1', is given by

$$K_1' = \frac{a_M - a_M^o}{a_M' - a_M} [H^+]$$

where

a_M = molar absorptivity for a mixture of the two absorbing species

a_M^o = molar absorptivity for unionized molecules

a_M' = molar absorptivity for ionized molecules

$[H^+]$ = molar concentration of hydrogen ion in the solution containing a mixture of the two species

If the length of the cell and the acid concentration remain constant throughout a series of measurements, the absorbance may be substituted for the molar absorptivity, giving

$$K_1' = \frac{A - A^o}{A' - A} [H^+]$$

where the superscripts retain their original meaning.

An equation similar in principle to the first can be written for the case of a second ionization constant.

$$K_2' = \frac{A - A'}{A'' - A} [H^+]$$

In this case

A = absorbance of a mixture of the two absorbing species

A' = absorbance of the singly ionized anion

A'' = absorbance of the doubly ionized anion

$[H^+]$ = molar hydrogen ion concentration in a solution containing a mixture of the two species

The latter equation is only applicable when the second ionization constant is significantly different from the first. This is necessary since the true absorption spectrum of the singly ionized species must be obtained. When these constants are not sufficiently different, K_1 and K_2 cannot be accurately determined by this method.

The experimental procedure called for in obtaining data for these equations involved a determination of the absorption spectrum of the ionic form, several mixtures of the ionized and nonionized forms having pH's near the pK value, and the unionized molecule.

From the same data taken for the first method of calculation, Carlson (6) developed a different and seemingly superior method, at least superior for this case. In this method the absorbance values of the various solutions prepared, measured at the wave length of the ionized form of the dioxime were plotted against the pH values of the corresponding solutions. This resulted in a curve not unlike that obtained in the titration of a strong acid with a strong base in which the pH is plotted against the volume of titrant added. An 'S' shaped curve was obtained. The midpoint of the break in the

curve corresponded to the point where the pH became identical with the pK':

$$pK' = pH - \log\frac{[salt]}{[acid]} \quad .$$

Back and Steenberg (1) have applied the Debye-Huckel theory to the calculation of the thermodynamic dissociation constant from the molar dissociation constant. The equation these authors developed in somewhat simplified form is

$$pK = pH + \log\frac{[salt]}{[acid]} + \frac{0.509\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}}$$

where μ is the ionic strength and the brackets indicate concentration. The ionic strength of the solutions used in the work described here was 0.1. This value results in a positive correction of 0.1, which is added to the molar dissociation constant to give the thermodynamic dissociation constant.

The acidic ionization constants of the three vic-dioximes studied by Banks and Carlson were found to be as follows:

	pK_1	pK_2
dimethylglyoxime	10.6 ± 0.1	11.9 ± 0.3
nioxime	10.6 ± 0.2	12.4 ± 0.5
heptoxime	10.7 ± 0.2	12.3 ± 0.5

The method used in the present work is similar to the second of the two methods described above. In this case a titration procedure was followed as opposed to the prepara-

tion of a series of solutions. The absorption peaks of the neutral and ionized species occur at 235 and 265 millimicrons, respectively (see Fig. 1). Twenty ml. of the $4x10^{-4}$ M solution of 2,2'-pyridildioxime were placed in a 200 ml. volumetric flask and diluted to volume with potassium chloride solution. This solution was then placed in a 400 ml. beaker equipped with a magnetic stirrer. The pH meter was set up to measure the pH of the solution. The absorbance of the solution was read against a water blank with the spectrophotometer at 235 and 265 millimicrons. A drop of the 6 M potassium hydroxide solution was added and the solution allowed 5 minutes to reach equilibrium. The pH and absorbance were read again and another drop of potassium hydroxide added. The samples to be read on the spectrophotometer were withdrawn from the body of the solution and placed in a curette with a dropping pipette. After the measurements were made the sample was returned to the body of solution. This procedure was continued until the pH reached a value too high to be determined with any accuracy by the pH meter and the electrode system.

C. Experimental Results

The spectra of a series of 2,2'-pyridildioxime solutions adjusted to different pH values were obtained with the Beckman DU spectrophotometer. The pH values of four portions of

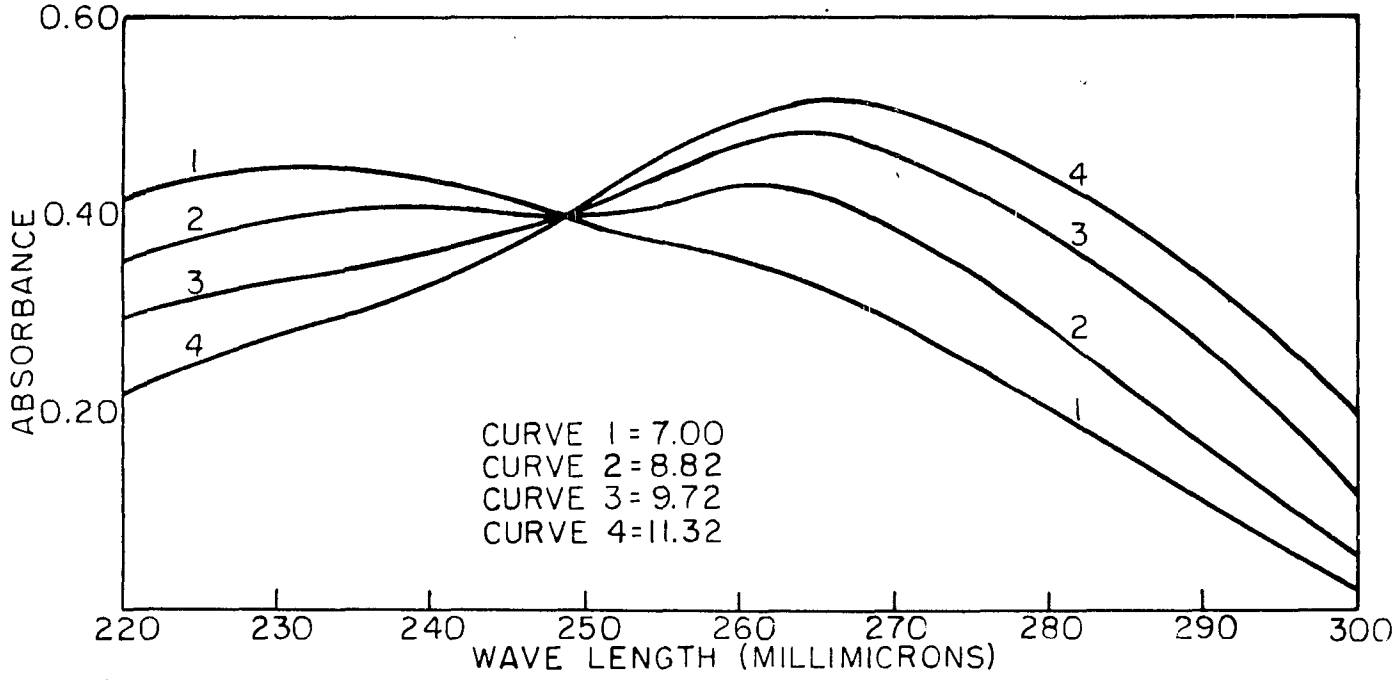


Fig. 1. Absorption curves illustrating effect of varying pH of 4×10^{-5} M solutions of 2,2'-pyridildioxime

the 4×10^{-5} M solution of 2,2'-pyridildioxime were adjusted with 6 M potassium hydroxide solution. The spectra of these solutions are shown in Fig. 1. Curves 1, 2, 3, and 4 correspond to pH values of 7.00, 8.82, 9.72, and 11.32, respectively. These spectra indicate that the absorption peak of the unionized molecule is at 235 millimicrons and that the absorption peak of the ionized form is at 265 millimicrons.

The previously described titration procedure was carried out at 25 ± 1°C. The results of these titrations are given in Table 1. The data from each titration at each wave length were combined and plotted (Figs. 2 and 3). In Figs. 2 and 3 it can be seen that there is evidence for a second break in the curves which would correspond to the second ionization constant. This break begins at a pH of about 12.6 and continues past 13. Since the measurement of pH in this region is not accurate, pK_2 was estimated to be about 13. No more precise measurement of this value was attempted. The values for pK_1' obtained from the curves averaged 9.14. To convert the molar dissociation constant to the thermodynamic dissociation constant the correction 0.1 was added and a pK_1 of 9.24 ± 0.1 was obtained.

Upon comparison of the values obtained in this work ($pK_1 = 9.24 \pm 0.1$, $pK_2 = 13$) with those obtained by Banks and Carlson (3) for the three common vic-dioximes (nioxime, heptoxime, and dimethylglyoxime), an important difference

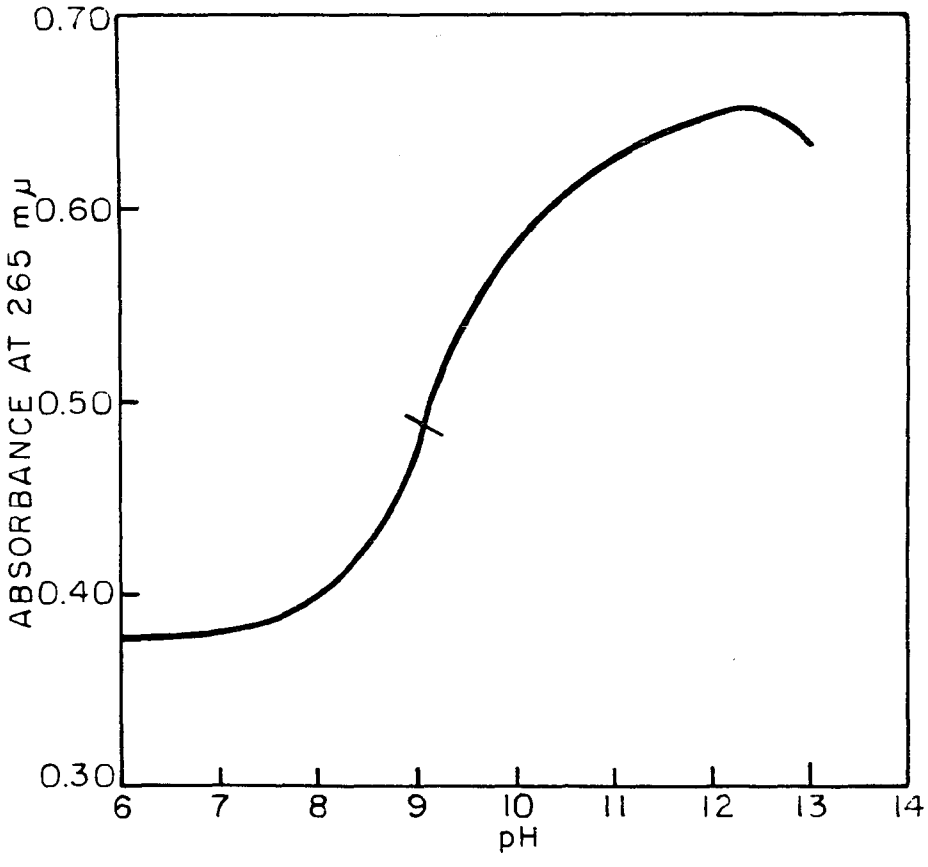


Fig. 2. Graphical determination of ionization constants of 2,2'-pyridildioxime (From data in Table 1)

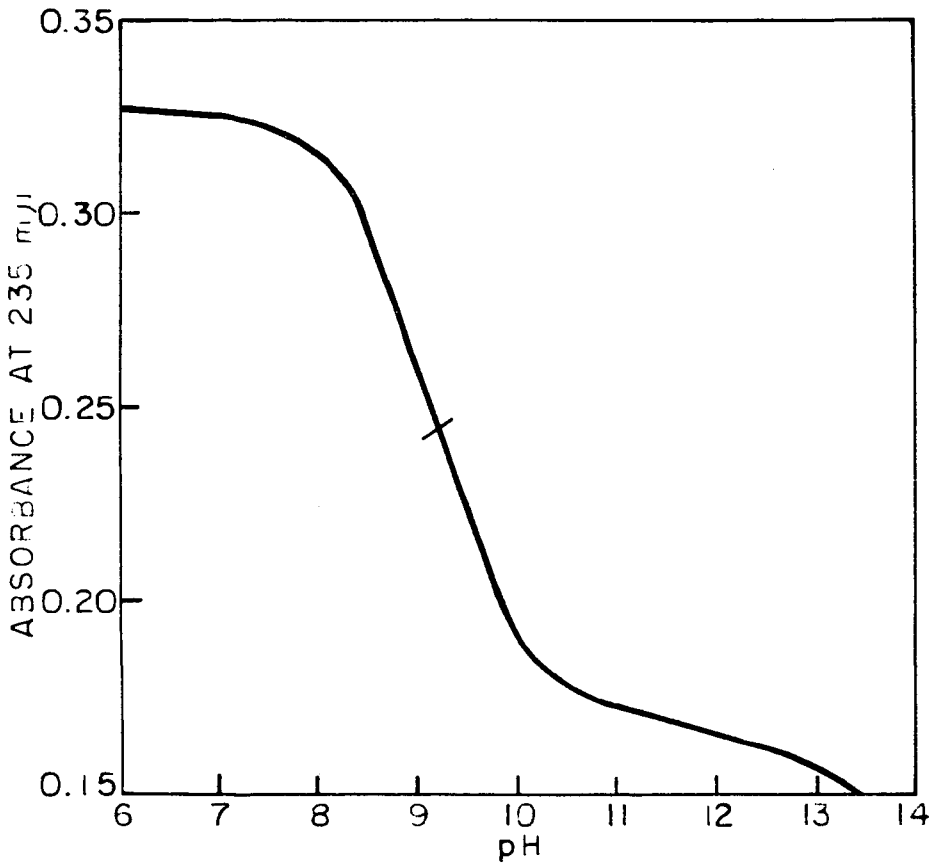


Fig. 3. Graphical determination of ionization constants of 2,2'-pyridildioxime (From data in Table 1)

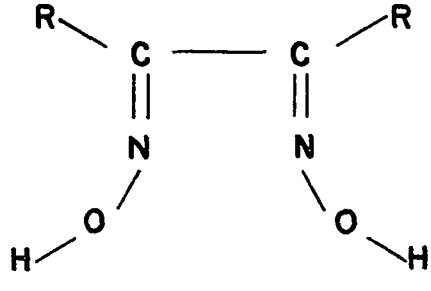
Table 1. Titration of 2,2'-pyridildioxime with potassium hydroxide

pH	A^{235}	A^{265}
	Solution I	
3.85	0.309	0.398
6.09	0.327	0.378
7.01	0.325	0.380
7.81	0.321	0.390
8.49	0.298	0.409
8.82	0.284	0.437
9.00	0.264	0.459
9.27	0.243	0.500
9.59	0.215	0.541
9.90	0.195	0.570
10.18	0.182	0.590
10.50	0.177	0.601
11.08	0.171	0.624
11.40	0.168	0.631
11.75	0.165	0.644
12.05	0.164	0.649
12.44	0.164	0.652
12.78	0.159	0.641
13.05	0.153	0.631
13.25	0.145	0.605
	Solution II	
6.23	0.327	0.378
6.89	0.325	0.380
7.70	0.322	0.389
8.20	0.309	0.400
8.68	2.84	0.422
8.92	0.268	0.450
9.09	0.255	0.474
9.20	0.245	0.494
9.41	0.230	0.525
9.76	0.206	0.560
10.09	0.185	0.583
10.40	0.178	0.600
10.77	0.174	0.612
11.19	0.170	0.625

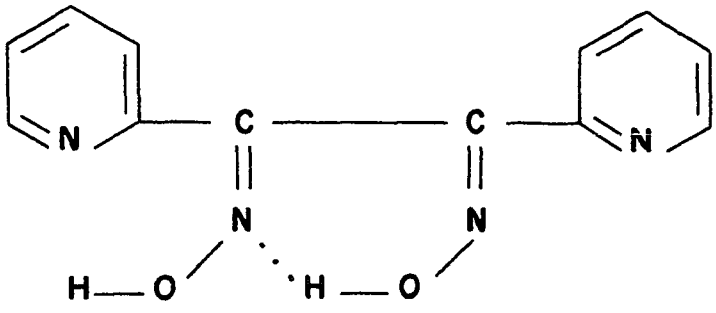
Table 1. (Continued)

pH	A^{235}	A^{265}
11.57	0.167	0.637
11.96	0.164	0.649
12.21	0.162	0.651
12.70	0.157	0.650
13.02	0.155	0.642

was noted. The pK_1 values for the three common vic-dioximes averaged 10.6 and the pK_2 values averaged 12.2. The first acid dissociation constant of 2,2'-pyridildioxime is an order of magnitude greater and the second acid dissociation constant is approximately an order of magnitude less than those obtained by Banks and Carlson. This discrepancy serves to confirm the supposition that the 2,2'-pyridildioxime is not in the anti- form as are the other vic-dioximes. The steric configuration of the anti- form may be represented by the following:



A possible structure of 2,2'-pyridildioxime which would explain the variance of the pK values is



If this were the case, one hydrogen would be released more readily and the second would be held more firmly than in the case of the anti- form.

V. DETERMINATION OF THE NATURE AND STABILITY OF SEVERAL IRON(II)-VIC-DIOXIME-AMINE COMPLEXES

A. Materials and Apparatus

1. Carbonate buffer

The buffer used in this work was prepared by dissolving 83.7 g. of potassium bicarbonate and 161 g. of potassium carbonate in enough water to make one liter of solution. Both of these reagents were Mallinckrodt 'A.R.' grade and contained less than 0.0005 per cent iron. This solution was approximately 2 M with respect to total carbonate and exhibited an apparent pH of 10.5 and a pH of 9.7 when diluted to 0.1 M.

2. Iron solution

A 0.01 M solution of iron was prepared by dissolving 0.5585 grams of pure electrolytic iron in hydrochloric acid, and diluting to one liter. This solution was used as a stock solution from which a 0.001 M iron solution was prepared. This solution contained both ferrous and ferric ions but since a powerful reducing agent was always used in conjunction with it, it was assumed that all the iron was converted to the ferrous form. This assumption was justified by passing a portion of the iron solution through a Jones reductor prior to use. The absorbance due to the ferrous

complex was the same whether the solution had been passed through the reductor or not.

3. Ammonia solution

A 0.1 M solution of ammonia was prepared by diluting reagent grade (Baker and Adamson) ammonium hydroxide with water to give the desired concentration. The concentration was checked by titration with standard hydrochloric acid.

4. Hydrazine solution

A 0.1 M solution of hydrazine was prepared by diluting anhydrous hydrazine obtained from the Matheson Company to give the desired concentration. The concentration was checked by titration with standard hydrochloric acid.

5. Ethylenediamine solution

A quantity of ethylenediamine obtained from the Matheson Company was purified by distillation over calcium oxide, retaining the fraction boiling at 116-117°C. A 0.1 M solution was prepared by dilution with water to the desired concentration. The concentration was checked by titration with standard hydrochloric acid.

6. Hydroxylamine solution

Baker and Adamson reagent grade hydroxylamine hydrochloride containing less than 0.0005 per cent iron was used to prepare this solution. A 0.1 M solution was prepared by dissolving a weighed portion of this material in water and adjusting the volume to give the desired concentration. The concentration was checked by adding an aliquot of the solution to a solution containing an excess of ferric ion and titrating the ferrous ion liberated with standard ceric sulfate.

7. Ethylamine solution

A water solution of ethylamine obtained from Eastman Kodak Company was used. A 0.1 M solution was prepared by dilution with the appropriate amount of water. The concentration was checked by titration with standard hydrochloric acid.

8. Sodium dithionite

A sample of this material obtained from Baker and Adamson was used throughout this work. No iron was detected in 0.1 gram of the sodium dithionite.

9. Dimethylglyoxime solution

A 0.01 M solution was prepared by weight from doubly recrystallized dimethylglyoxime. A few drops of 6 M potas-

sium hydroxide were used to effect dissolution. This solution was standardized by adding an excess of Ni(II) sulfate to ammonium acetate buffered aliquots, then digesting, filtering, drying, and weighing according to the procedure given by Diehl and Smith (10). The solution was used immediately after standardization. The concentration as determined was 0.00996 M.

10. Nioxime solution

A 0.01 M solution was prepared by weight from doubly recrystallized nioxime. The solution was standardized by adding an excess of Ni(II) sulfate to ammonium acetate buffered aliquots, then digesting, filtering, drying, and weighing according to the procedure given by Voter and Banks (41). The concentration as determined was 0.01005 M.

11. Heptoxime solution

A 0.01 M solution was prepared by weight from doubly recrystallized heptoxime. The solution was standardized by adding an excess of Ni(II) sulfate to ammonium acetate buffered aliquots, then digesting, filtering, drying, and weighing according to the procedure given by Voter and Banks (41). The concentration as determined was 0.01006 M.

12. 2,2'-pyridildioxime solution

A 0.01 M solution was prepared by weight from the purified material described in Section III-C. Potassium hydroxide was added dropwise to effect dissolution. A $1x10^{-3}$ M solution was prepared as needed by diluting the 0.01 M solution.

13. Measurement of pH

A Beckman model G pH meter was used for all pH measurements. A Beckman type E-2 shielded glass electrode and a Beckman saturated calomel electrode were used in conjunction with this meter.

14. Spectrophotometer

A Beckman model B spectrophotometer was used to make all optical measurements in this section. All readings were made against a water blank.

15. Water

Distilled, deionized water was used to prepare all solutions.

B. Experimental Procedure

1. Preliminary considerations

In order to more fully explain the nature of the iron-amine-vic-dioxime complexes it is necessary to point out cer-

tain facts about them. The complexes are inert in varying degrees, depending primarily on which vic-dioxime is involved. The Fe(II) complexes of the three well known vic-dioximes studied - dimethylglyoxime, nioxime, and heptoxime - reach a stable state in an average of one half hour. The complexes of 2,2'-pyridildioxime require two to four hours to reach equilibrium at a pH of 9.5, depending on the amine used to form the complex. After equilibrium is attained the color is stable for several days until the reducing agent begins to decompose.

When one of the three well known vic-dioximes was mixed with ferrous iron in a solution buffered at a pH of 9.5 which contains the reducing agent sodium dithionite, a yellow color was observed. As the concentration of the vic-dioxime was increased the color observed became more reddish. These observations were also made by Vaubel (37). It was assumed that the yellow color was due to a complex involving only iron(II) and the vic-dioxime. The nature and cause of the red color was attributed to slow decomposition of the excess vic-dioxime to liberate hydroxylamine which assumed the role of the amine in forming the ternary complex.

Another factor encountered was the presence of several different complexes shortly after mixing the reactants. When Fe(II) is added to a solution buffered at a pH of 9.5 containing sodium dithionite, an amine, and a vic-dioxime, a

blue-red color is first observed which gradually changes to red. This was observed in all cases but the transition was particularly marked in the case of the 2,2'-pyridildioxime complexes since the attainment of equilibrium was so much slower. A study of these transitions was made and will be described in more detail later.

The stability constants measured in this section are apparent stability constants. The concept of apparent constants has been used extensively by Schwarzenbach (28). The primary difference between an apparent constant and a true or thermodynamic constant is that an apparent constant contains no hydrogen ion term and thus is pH dependent. Since chelate formation involves the substitution of a metal ion for a hydrogen ion, the pH of the system is of primary importance. If the acidic ionization constants of the chelating agent are known and the nature of the complex is thoroughly understood, the thermodynamic constant can be calculated from the apparent constant. If, however, the complex is always formed at a certain pH, then the concept of the apparent constant is quite useful. In the case of Schwarzenbach's work, the metal ion indicators he studied are almost always used at the same pH. In addition there is some question about the exact nature of the chelate forming reaction. The same situation is encountered in the present work. There is a narrow pH range at which the formation of the complex

is most complete. This then is the range of interest and the only possible range of use for analytical purposes. In addition to this consideration there is a serious complication due to the mode of complex formation which would render the determination of any thermodynamic equilibrium constants very difficult.

2. pH dependence

The relation of the pH to the absorbance of a metal ion complex is a very important consideration in the utilization of the complex in a spectrophotometric method. The pH effect in the Fe(II)-ammonia-nioxime system was studied by Matthews (23) who showed that the maximum color was only obtained when the pH was 9.5 or higher. The pH dependence of the Fe(II)-2,2'-pyridildioxime system in conjunction with various amines was studied.

To a 200 ml. beaker equipped with a magnetic stirrer were added 5 ml. of 0.01 M 2,2'-pyridildioxime and 5 ml. of a 0.1 M solution of an amine. The solution was then diluted to approximately 100 ml. and the pH adjusted to 4.0 by dropwise addition of hydrochloric acid. At this point 2 ml. of 1×10^{-3} M Fe(II) chloride solution were added along with 0.1 g. of sodium dithionite. The pH was then slowly increased by dropwise addition of 6 M potassium hydroxide. After each addition the solution was stirred for fifteen minutes. The

pH and absorbance of the solution were then determined and another addition of the potassium hydroxide solution made.

3. Method of continuous variations

The main objective of this portion of the investigation was the determination of the ratio of iron to 2,2'-pyridildioxime immediately after formation of the complex and also several hours later. As previously mentioned there is a change in color from that observed immediately after mixing the reactants to that observed after some time has elapsed. The method of continuous variations seemed particularly applicable to this situation. This method, proposed by Job (18) in his researches on the ammonia complexes of divalent metals, was extended to more complicated systems by Vosburgh and Cooper (38).

The method of continuous variation is based on the variance in the absorbance of a series of solutions in which the total mole fraction of two variable constituents is kept fixed. A series of solutions was made in which the molar concentration of iron plus 2,2'-pyridildioxime was varied from 0 to 2×10^{-4} M. Sufficient iron was added to make the total molar concentration of iron plus 2,2'-pyridildioxime 2×10^{-4} in each of the solutions. Each of the solutions also contained 0.1 g. of sodium dithionite, 5 ml. of carbonate buffer, and 5 ml. of 0.1 M ammonia solution. The series of

solutions was diluted to 100 ml. in volumetric flasks. Exactly ten minutes after the reactants were mixed the absorbance of each solution was measured at 530, 550, and 570 millimicrons. The solutions were then allowed to stand for six hours and then the absorbances at 510, 530, and 550 millimicrons were determined. The absorbance values measured at each wave length were plotted against the mole fraction of 2,2'-pyridildioxime.

The ratio of 2,2'-pyridildioxime to Fe(II) was calculated from the equation

$$n = \frac{X}{1 - X} .$$

The values of X were obtained from the plots prepared as described above at the point where the two straight lines intersect. The n corresponds to the number of 2,2'-pyridildioxime molecules associated with each ferrous ion according to the reaction

$$Fe^{++} + n(2,2'\text{-pyr}) = Fe(2,2'\text{-pyr})_n .$$

4. Conformity to Beer's law

The method used for the determination of the apparent stability constants requires a linear relationship between the concentration of the colored species and its absorbance. This linear relationship is generally known as Beer's law.

Matthews (23) demonstrated that the Fe(II)-nioxime system obeys Beer's law in conjunction with any amine used. In the present work, conformity to Beer's law was checked in all cases where an apparent stability constant was to be determined.

Five ml. of carbonate buffer, 0.1 g. of sodium dithionite, 50 ml. of a 1×10^{-2} M solution of the vic-dioxime being studied, and 5 ml. of a 0.1 M solution of the amine being studied were placed in a 100 ml. volumetric flask. Five such flasks were prepared for each combination of amine and vic-dioxime. Sufficient Fe(II) chloride solution was added to make the iron concentrations 5×10^{-6} M, 1×10^{-5} M, 2×10^{-5} M, 5×10^{-5} M, and 1×10^{-4} M in the series of volumetric flasks. Readings were taken after four hours at the wave length of maximum absorbance and these values were plotted against the corresponding Fe(II) concentration.

5. Determination of the apparent stability constants

The method of establishing the apparent stability constants is primarily based on the method of Diehl and Sealock (9), commonly known as the log ratio method. The reaction of Fe(II) with the vic-dioximes may be represented by the equation

$$Fe^{++} + n\,[D] = FeD_n \qquad (1)$$

The role of the amine in this reaction was neglected since the amine was present in great excess. Matthews (23) demonstrated that the amine is very loosely bound. D represents all species of the vic-dioxime present except that which is combined with the iron. The apparent stability constant may be represented as

$$K = \frac{[FeD_n]}{[Fe][D]^n} \qquad (2)$$

where the brackets signify equilibrium concentration.

By converting Equation 2 to logarithmic form, we obtain,

$$\log K = \log\frac{[FeD_n]}{[Fe][D]^n} = \log\frac{[FeD_n]}{[Fe]} - n\log[D] \quad . \qquad (3)$$

Rearranging Equation 3 to the equation of a straight line, we obtain,

$$\log\frac{[FeD_n]}{[Fe]} = n\log[D] + \log K \quad . \qquad (4)$$

When $\log[D]$ is plotted against $\log\frac{[FeD_n]}{[Fe]}$, the slope is equal to 'n' and the y intercept is log K.

In this procedure, the concentration of the Fe(II) was held constant while the concentration of the vic-dioxime was varied. All the iron was assumed to be in the complexed form when the vic-dioxime was in great excess. The absorbance due to the complex measured in this limiting case was then assumed to be equivalent to all the iron present. In a case

where the vic-dioxime was not present in great excess the ratio between the absorbance measured and the difference between the absorbance of the limiting case and the absorbance measured was equal to $\frac{[FeD_n]}{[Fe]}$. The value of [D] was obtained by subtracting the calculated concentration of $[FeD_n]$ from the analytical concentration (D') of the vic-dioxime added. The solutions used in the section were all buffered at a pH of 9.6-9.75.

The preparation of the solutions in this section was done according to the following procedure. All solutions were prepared in 100 ml. volumetric flasks. To each flask was added 5 ml. of carbonate buffer solution and 5 ml. of amine solution which yielded a final carbonate concentration of 0.1 M and a final amine concentration of 5×10^{-3} M. The desired amount of 1×10^{-2} or 1×10^{-3} M vic-dioxime solution was then added along with 0.1 g. of solid sodium dithionite. At this point the solutions were diluted to about 50 ml. and mixed to dissolve the sodium dithionite. To each flask, 2 ml. of the 1×10^{-3} M solution of Fe(II) chloride were added which yielded a final iron concentration of 2×10^{-5} M when the solution was diluted to volume. The solutions were then allowed to stand for the desired length of time before their absorbances were measured.

The 0.1 M carbonate buffer at a pH of 9.7 resulted in an ionic strength of 0.144. The temperature was held to 25 ± 2°C.

C. Experimental Results

1. The iron-vic-dioxime complex

There is definite evidence for the formation of a complex involving only Fe(II) and a vic-dioxime. Curve 1 in Fig. 4 illustrates the spectrum of this complex. As the concentration of nioxime was increased there was a shift of the peak wave length and an increase in absorbance (curves 2, 3, 4, 5, 6, 7). The actual nioxime concentrations used are given in Table 2. The concentration of Fe(II) is the same in each case. The solution yielding the spectrum shown by curve 8 was identical to the solution yielding curve 7 except that 5 ml. of 0.1 M hydroxylamine solution were added. All eight solutions were prepared in 100 ml. volumetric flasks.

It can be seen from the spectra in Fig. 4 that there was a different complex present when the nioxime was present in high concentration. It is also evident that the spectrum of the solution containing the highest concentration of nioxime is the same as that containing the hydroxylamine. The peaks observed did not approach a limiting absorbance so it was assumed that the complex was quite weak. An attempt was made to apply the method of continuous variations to the

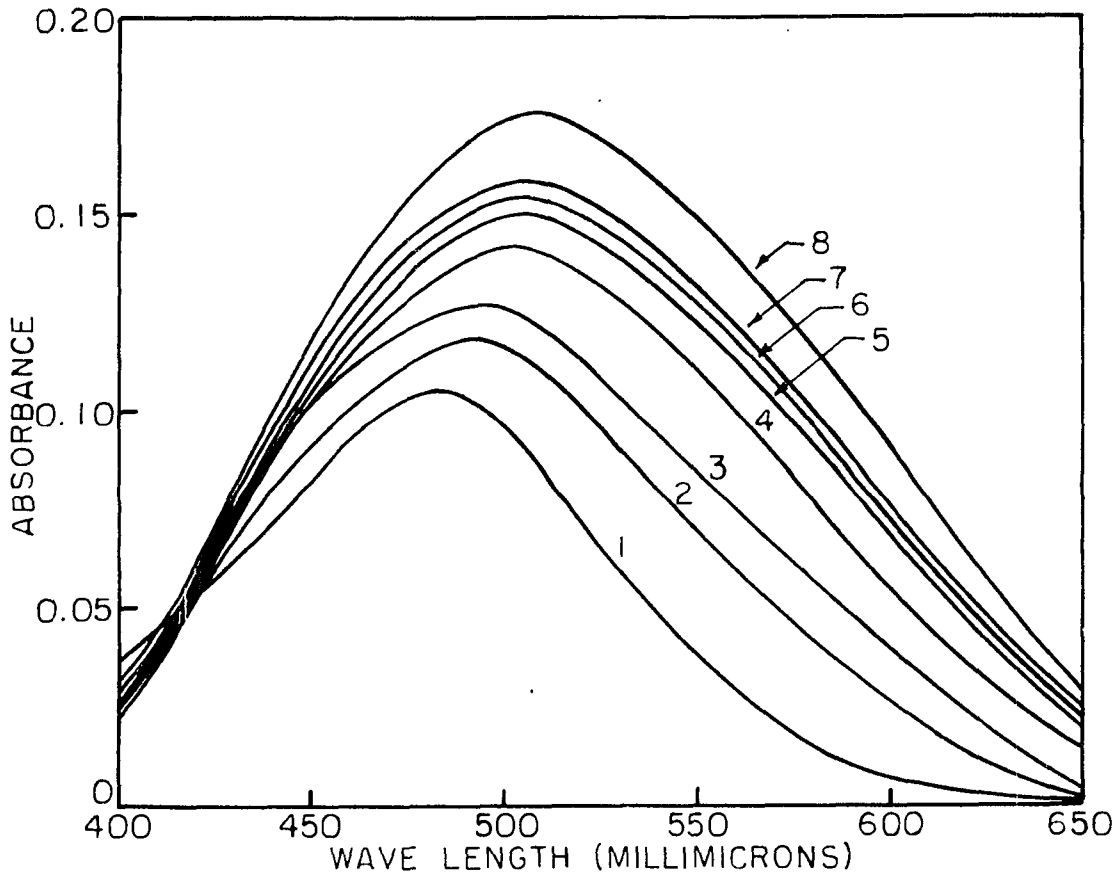


Fig. 4. Absorption curves illustrating effect of increasing nioxime concentration in a buffered iron(II) chloride solution (Numbers correspond to solutions described in Table 2)

Table 2. Solutions used to illustrate the spectral shift of the Fe(II)-nioxime complex[a]

Curve number	Concentration of nioxime	pH
1	2×10^{-5} M	9.68
2	5×10^{-5} M	9.71
3	1×10^{-4} M	9.73
4	5×10^{-4} M	9.69
5	1×10^{-3} M	9.70
6	2×10^{-3} M	9.67
7	5×10^{-3} M	9.74
8[b]	5×10^{-3} M	9.68

[a]All solutions contained 5 ml. of carbonate buffer, 0.1 g. of sodium dithionite, and 2 ml. of 1×10^{-3} M Fe(II) solution in 100 ml. total volume.

[b]This solution contained 5 ml. of hydroxylamine hydrochloride solution.

Fe(II)-nioxime system in the absence of any amine but the results were so erratic nothing was learned. Results almost identical with those shown in Fig. 4 for nioxime were obtained with dimethylglyoxime and heptoxime.

A similar experiment was performed with 2,2'-pyridildioxime. In this case there was no shift in the wave length of maximum absorbance (515 millimicrons) with an increase in the concentration of the dioxime. No limiting absorbance

was reached by increasing the 2,2'-pyridildioxime concentration as high as $1x10^{-2}$ M. It was evident that the excess 2,2'-pyridildioxime was also serving as an amine in this reaction.

One conclusion from this study was that Fe(II) does form a weak complex with the vic-dioximes in the absence of any amine. It was also concluded that any quantitative work was impossible because of the slight decomposition of the vic-dioximes to liberate small but unknown amounts of hydroxylamine into the system.

2. pH dependence of some Fe(II)-2,2'pyridildioxime-amine systems

Fig. 5 gives the results of the determination of the variation in absorbance of several Fe(II)-2,2'-pyridildioximeamine complexes as the pH of the system was increased. In curve 1 the amine used was ammonia, in curve 2, pyridine, in curve 3, hydrazine, and in curve 4, ethylamine. It was observed that although the curves approach different limiting absorbances, the pH giving maximum absorbance was about the same in each case. It was also observed that when the pH of each solution exceeded 10.3 the absorbance began to decrease. It is evident from this study that the complexes reach maximum stability at a pH between 9.5 and 10.3.

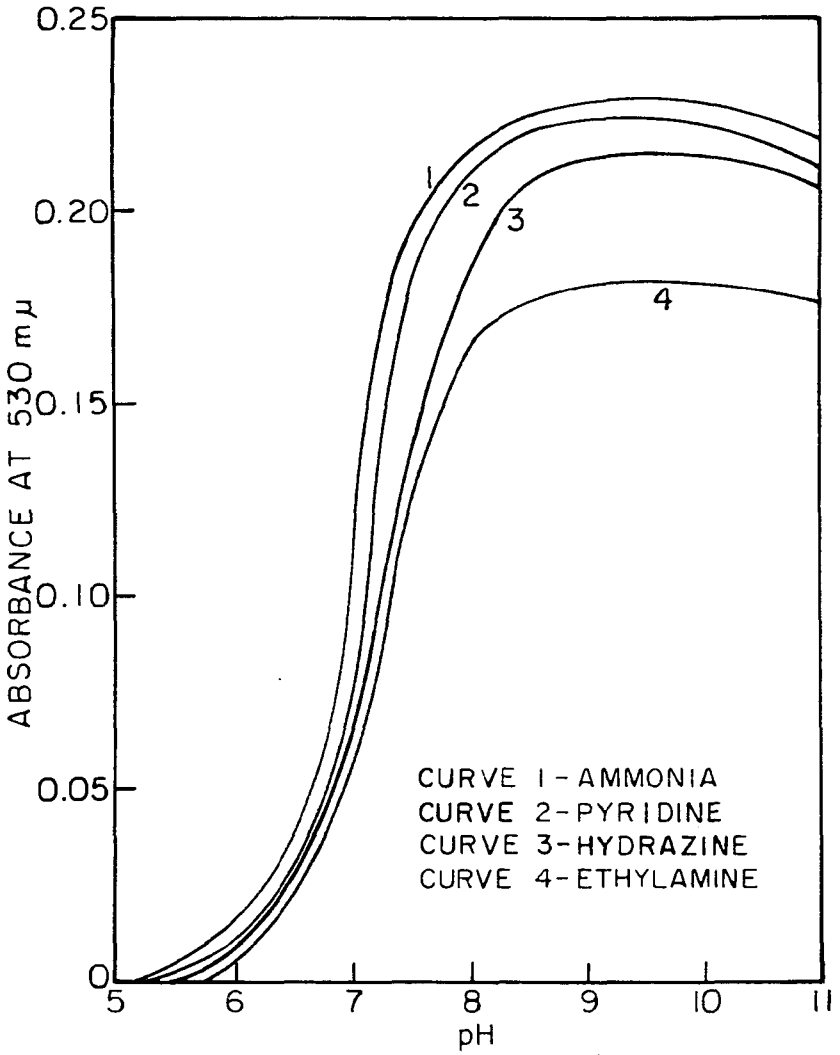


Fig. 5. Stability of several iron(II)-2,2'-pyridildioxime-amine complexes as a function of pH

3. Time dependence of the Fe(II)-2,2'-pyridildioxime-ammonia system

Fig. 6 illustrates the change in the spectrum of the Fe(II)-2,2'-pyridildioxime-ammonia system upon standing. The spectrum represented by Curve 1 was determined approximately 15 minutes after the initial development of the color. Curve 2 was obtained from the same solution six hours later. This change can be observed with the naked eye.

The same system was also studied in a somewhat different manner. The necessary reactants were mixed and absorbance measurements made periodically at 555 and 530 millimicrons. The values obtained at 555 millimicrons increased in five minutes to a limiting value and remained at this value for ten minutes. The absorbance values then began to drop very slowly over a period of four hours. After four hours no further change in the absorbance was noted for twelve to fifteen hours when a slight decrease began. The values obtained at 530 millimicrons increased rapidly for the first five minutes, then continued to increase slowly for the next four hours when they became constant. This value remained unchanged for twelve to fourteen hours when a slow decrease was noted.

This phenomenon was also observable with the other vic-dioximes under study. The transition in these cases was much more rapid, however, and the determination of the spectra

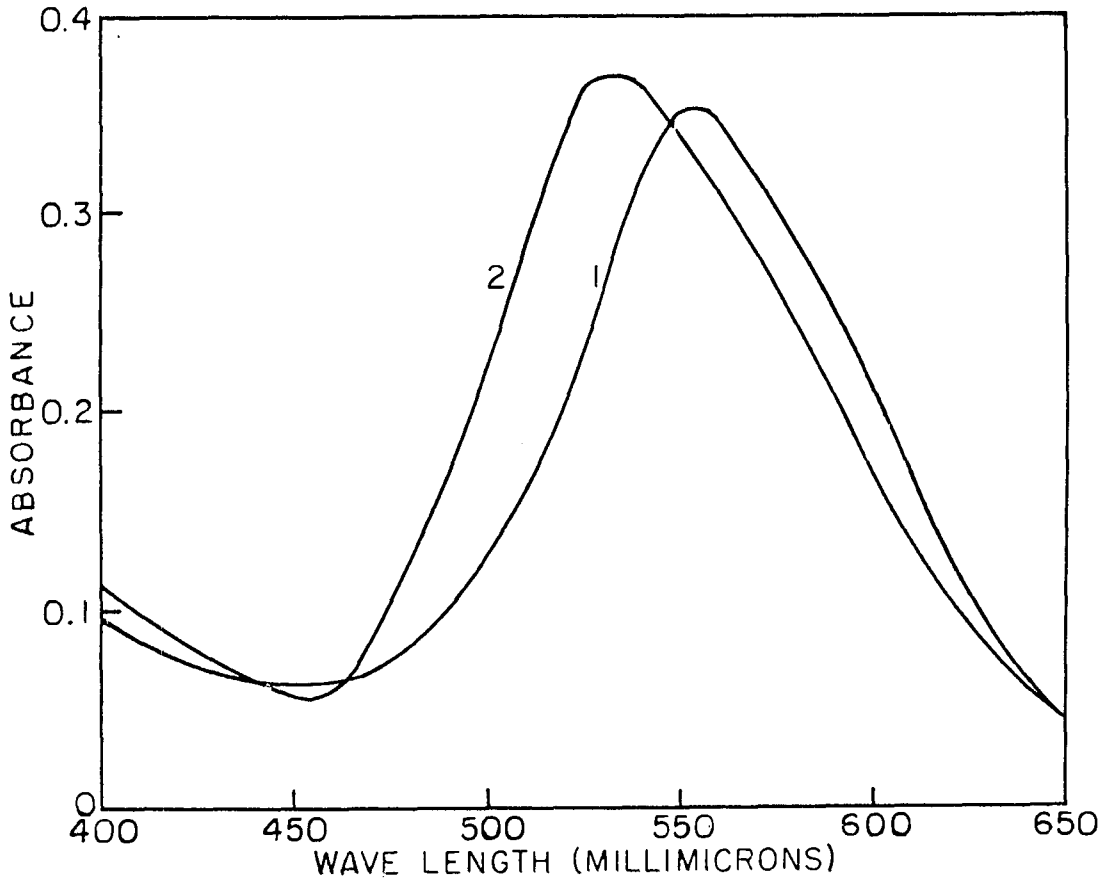


Fig. 6. Absorption curves illustrating the spectral changes in the iron(II)-2,2'-pyridildioxime-ammonia system upon standing for six hours

was found to be pointless since the systems were changing so rapidly.

4. The method of continuous variations applied to the Fe(II)-2,2'-pyridildioxime-ammonia system

Since this system reached equilibrium more slowly than any other encountered, it was chosen for this study. The procedure previously described in Section V-B-3 was followed. The solutions were prepared one at a time so that the absorbance of each was determined exactly 10 minutes after the addition of the Fe(II) chloride solution. The composition of each solution is given in Table 3. The absorbances measured are given in Tables 3 and 4. A plot of the absorbances measured after ten minutes is shown in Fig. 7, and a plot of the absorbances measured after 6 hours is shown in Fig. 8.

In Fig. 7 the value of 'x' obtained was 0.67 which yielded an 'n' value of 2.03. This indicates a two to one ratio of 2,2'-pyridildioxime to Fe(II) when the reactants were first mixed. In Fig. 8 the value of 'x' obtained was 0.51 which yielded an 'n' value of 1.04. This indicated a one to one ratio after the system had reached equilibrium.

5. Conformity to Beer's law

All four vic-dioximes under study were examined to determine whether they obeyed Beer's law over the region of inter-

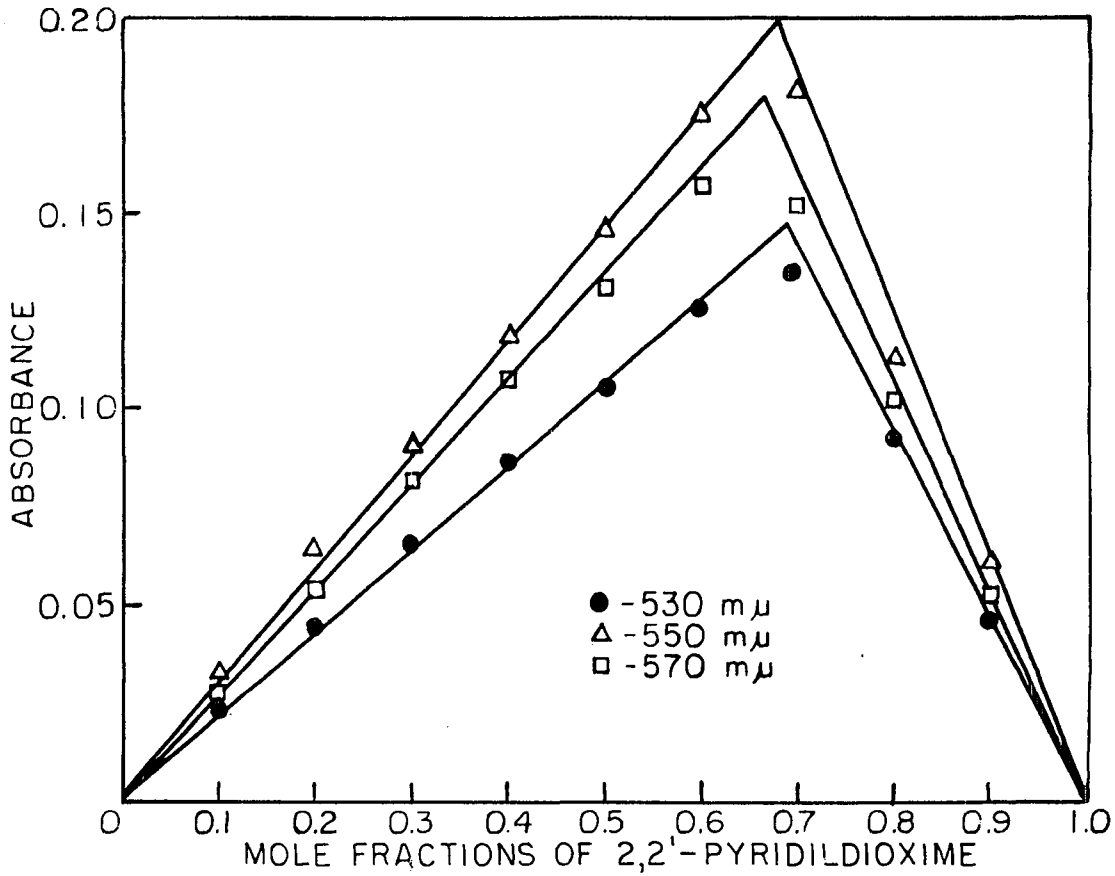


Fig. 7. Continuous variations. Iron(II)-2,2'-pyridildioxime-ammonia system after ten minutes

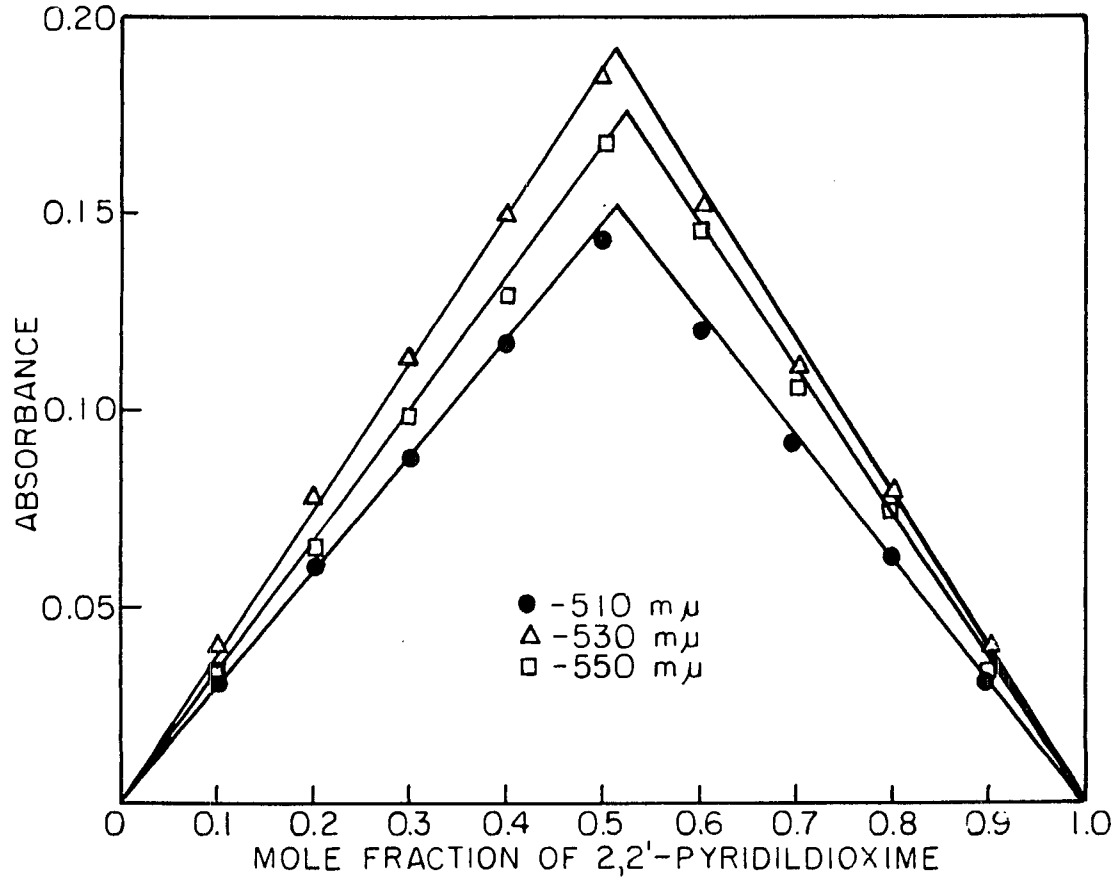


Fig. 8. Continuous variations. Iron(II)-2,2'-pyridildioxime-ammonia system after six hours

Table 3. Method of continuous variations for the Fe(II)-2,2'-pyridildioxime-ammonia system[a]

Solution number	Concentration of 2,2'-pyridildioxime	A^{530}	A^{550}	A^{570}
1	0	0.003	0.003	0.003
2	2×10^{-5} M	0.024	0.033	0.030
3	4×10^{-5} M	0.045	0.064	0.055
4	6×10^{-5} M	0.067	0.091	0.083
5	8×10^{-5} M	0.088	0.118	0.108
6	1×10^{-4} M	0.106	0.146	0.133
7	1.2×10^{-4} M	0.126	0.175	0.159
8	1.4×10^{-4} M	0.137	0.181	0.153
9	1.6×10^{-4} M	0.093	0.114	0.102
10	1.8×10^{-4} M	0.047	0.061	0.052
11	2.0×10^{-4} M	0.001	0.000	0.000

[a]All solutions read after exactly 10 minutes

Table 4. Method of continuous variations for the Fe(II)-2,2'-pyridildioxime-ammonia system[a]

Solution number	A^{510}	A^{530}	A^{550}
1	0.003	0.003	0.004
2	0.031	0.040	0.036

[a]All solutions are the same as those described in Table 3. The absorbances were read after 6 hours.

Table 4. (Continued)

Solution number	A^{510}	A^{530}	A^{550}
3	0.060	0.078	0.071
4	0.088	0.114	0.100
5	0.118	0.149	0.132
6	0.144	0.185	0.167
7	0.120	0.152	0.145
8	0.092	0.112	0.105
9	0.063	0.078	0.074
10	0.033	0.039	0.032
11	0.001	0.001	0.001

est. The results of this study are found in Tables 5, 6, 7, and 8. The data for the heptoxime and 2,2'-pyridildioxime systems has been plotted in Fig. 9. The molar absorptivities determined are tabulated in Table 9.

All systems studied obeyed Beer's law over the region of interest. In the determination of the apparent stability constants an Fe(II) concentration of 2×10^{-5} M was employed. In this region of concentration the results were linear within the reading error of the spectrophotometer.

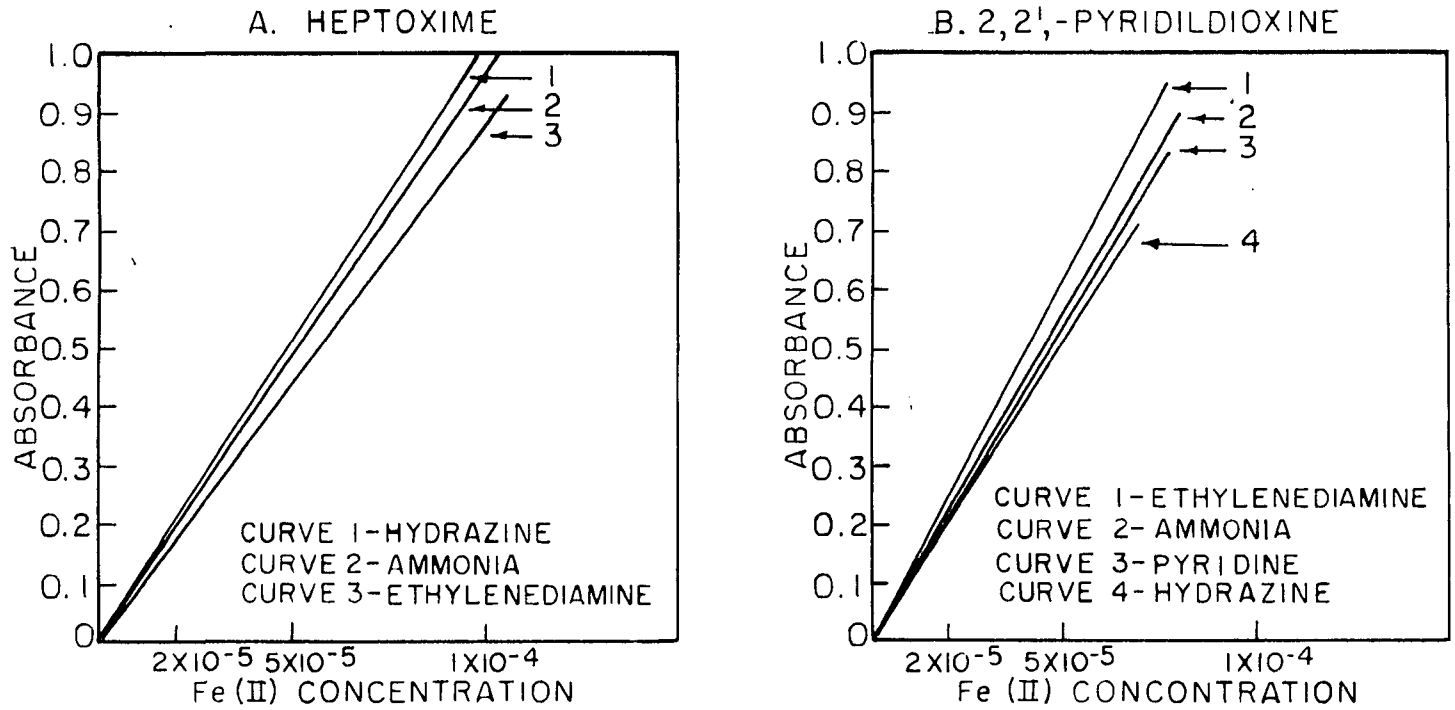


Fig. 9. Beer's law plots

Table 5. Data from Beer's law study with heptoxime

Fe(II) concentration	$A^{520}_{ammonia}$	$A^{550}_{hydrazine}$	$A^{550}_{ethylenediamine}$
$5x10^{-6}$ M	0.053	0.056	0.047
$1x10^{-5}$ M	0.102	0.107	0.089
$2x10^{-5}$ M	0.200	0.212	0.180
$5x10^{-5}$ M	0.486	0.521	0.441
$1x10^{-4}$ M	0.95	1.0	0.88

Table 6. Data from Beer's law study with nioxime

Fe(II) concentration	$A^{530}_{ammonia}$	$A^{530}_{hydrazine}$	$A^{550}_{ethylenediamine}$
$5x10^{-6}$ M	0.043	0.043	0.047
$1x10^{-5}$ M	0.087	0.082	0.085
$2x10^{-5}$ M	0.173	0.159	0.167
$5x10^{-5}$ M	0.432	0.390	0.420
$1x10^{-4}$ M	0.860	0.750	0.840

Table 7. Data from Beer's law study with dimethylglyoxime

Fe(II) concentration	$A^{520}_{ammonia}$	$A^{500}_{hydrazine}$	$A^{520}_{ethylenediamine}$
$5x10^{-6}$ M	0.043	0.034	0.031
$1x10^{-5}$ M	0.088	0.070	0.061
$2x10^{-5}$ M	0.172	0.135	0.121
$5x10^{-5}$ M	0.428	0.337	0.315
$1x10^{-4}$ M	0.840	0.650	0.647

Table 8. Data from Beer's law study with 2,2'-pyrdildioxime

Fe(II) concentration	A^{550}_{en}	$A^{530}_{NH_3}$	$A^{530}_{pyridine}$	$A^{530}_{N_2H_4}$
$5x10^{-6}$ M	0.063	0.057	0.056	0.052
$1x10^{-5}$ M	0.123	0.115	0.110	0.105
$2x10^{-5}$ M	0.247	0.228	0.220	0.208
$5x10^{-5}$ M	0.615	0.566	0.546	0.515
$1x10^{-4}$ M	1.22	1.12	1.08	1.02

Table 9. Molar absorptivities of Fe(II)-vic-dioxime-amine systems

System	Molar absorptivity
Heptoxime-ammonia	10000
Heptoxime-hydrazine	10600
Heptoxime-ethylenediamine	9000
Nioxime-ammonia	8650
Nioxime-hydroxylamine	9650
Nioxime-ethylenediamine	8350
Dimethylglyoxime-ammonia	8600
Dimethylglyoxime-hydrazine	6750
Dimethylglyoxime-ethylenediamine	6000
2,2'-pyridildioxime-ammonia	11400
2,2'-pyridildioxime-ethylenediamine	12350
2,2'-pyridildioxime-pyridine	11000
2,2'-pyridildioxime-hydrazine	10400

6. Apparent stability constants

(a) Heptoxime. The Fe(II) complexes of heptoxime were studied in conjunction with ammonia, hydrazine, and ethylenediamine. Absorbance readings were made on each solution at wave lengths near the absorption maximum. The results with

ammonia, hydrazine, and ethylenediamine are tabulated in Tables 10, 11, and 12, respectively.

In order to make the method of calculation clear, Table 13 contains a sample of the calculations made at one wave length for the Fe(II)-heptoxime-hydrazine system. In Fig.

Table 10. Log-ratio method for Fe(II)-heptoxime-ammonia[a]

Concentration of heptoxime	A^{500}	A^{520}	A^{540}
5×10^{-5} M	0.134	0.146	0.137
5×10^{-5} M	0.133	0.145	0.137
5×10^{-5} M	0.134	0.145	0.138
1×10^{-4} M	0.160	0.172	0.164
1×10^{-4} M	0.162	0.173	0.162
1×10^{-4} M	0.159	0.170	0.163
2×10^{-4} M	0.179	0.190	0.182
2×10^{-4} M	0.176	0.185	0.180
2×10^{-4} M	0.177	0.190	0.179
5×10^{-4} M	0.186	0.198	0.190
5×10^{-4} M	0.187	0.201	0.191
5×10^{-4} M	0.188	0.201	0.191
1×10^{-3} M	0.190	0.203	0.196
1×10^{-3} M	0.191	0.204	0.195
1×10^{-3} M	0.192	0.204	0.194
2×10^{-3} M	0.195	0.206	0.198
2×10^{-3} M	0.195	0.209	0.198
2×10^{-3} M	0.194	0.208	0.199
5×10^{-3} M	0.193	0.208	0.199
5×10^{-3} M	0.194	0.208	0.198

[a]Absorbances determined after five hours

Table 11. Log-ratio method for Fe(II)-heptoxime-hydrazine[a]

Concentration of heptoxime	A^{520}	A^{530}	A^{540}
5×10^{-5} M	0.106	0.111	0.114
5×10^{-5} M	0.103	0.109	0.111
5×10^{-5} M	0.105	0.110	0.114
1×10^{-4} M	0.142	0.145	0.149
1×10^{-4} M	0.140	0.144	0.147
1×10^{-4} M	0.139	0.142	0.147
2×10^{-4} M	0.165	0.169	0.174
2×10^{-4} M	0.165	0.168	0.174
2×10^{-4} M	0.164	0.167	0.174
5×10^{-4} M	0.191	0.199	0.204
5×10^{-4} M	0.189	0.196	0.202
5×10^{-4} M	0.189	0.198	0.202
1×10^{-3} M	0.196	0.206	0.213
1×10^{-3} M	0.198	0.207	0.212
1×10^{-3} M	0.197	0.206	0.213
2×10^{-3} M	0.201	0.210	0.217
2×10^{-3} M	0.202	0.211	0.218
2×10^{-3} M	0.202	0.212	0.218
5×10^{-3} M	0.205	0.214	0.221
5×10^{-3} M	0.205	0.215	0.222

[a]Absorbances determined after six hours

Table 12. Log-ratio method for Fe(II)-heptoxime-ethylenediamine[a]

Concentration of heptoxime	A^{530}	A^{540}	A^{550}	A^{560}	A^{570}	A^{580}
2×10^{-5} M	0.077	0.090	0.109	0.120	0.125	0.121
5×10^{-5} M	0.075	0.089	0.110	0.120	0.123	0.118

[a]Absorbances determined after six hours

Table 12. (Continued)

Concentration of heptoxime	A^{530}	A^{540}	A^{550}	A^{560}	A^{570}	A^{580}
5×10^{-5} M	0.126	0.148	0.177	0.188	0.189	0.184
5×10^{-5} M	0.123	0.145	0.174	0.190	0.192	0.187
1×10^{-4} M	0.135	0.159	0.190	0.204	0.206	0.203
1×10^{-4} M	0.135	0.156	0.187	0.203	0.206	0.202
2×10^{-4} M	0.141	0.164	0.196	0.212	0.213	0.209
2×10^{-4} M	0.140	0.164	0.195	0.209	0.211	0.208
5×10^{-4} M	0.144	0.167	0.200	0.217	0.217	0.213
5×10^{-4} M	0.146	0.168	0.200	0.216	0.217	0.213
1×10^{-3} M	0.153	0.173	0.198	0.211	0.217	0.213
1×10^{-3} M	0.150	0.168	0.201	0.217	0.212	0.210
2×10^{-3} M	0.161	0.179	0.202	0.203	0.200	0.198
2×10^{-3} M	0.160	0.179	0.200	0.198	0.199	0.196
5×10^{-3} M	0.175	0.188	0.201	0.186	0.183	0.176
5×10^{-3} M	0.169	0.189	0.202	0.191	0.186	0.181

Table 13. Calculation for Fe(II)-heptoxime-hydrazine system

Concentration of heptoxime	A^{530}	FeD_n	Fe	$\frac{FeD_n}{Fe}$	D
5×10^{-5} M	0.110	1.02×10^{-5}	9.8×10^{-6}	1.04	3.98×10^{-5}
1×10^{-4} M	0.144	1.34×10^{-5}	6.6×10^{-6}	2.03	8.70×10^{-5}
2×10^{-4} M	0.168	1.56×10^{-5}	4.4×10^{-6}	3.54	1.84×10^{-4}
5×10^{-4} M	0.198	1.84×10^{-5}	1.6×10^{-6}	11.5	4.82×10^{-4}
1×10^{-3} M	0.206	1.92×10^{-5}	8.3×10^{-7}	22.1	9.80×10^{-4}
2×10^{-3} M	0.211	1.96×10^{-5}	3.8×10^{-7}	51.5	1.98×10^{-3}
5×10^{-3} M	0.215				

10 the absorbances measured are plotted against the concentration of heptoxime for the Fe(II)-heptoxime-hydrazine system. This was done to justify the assumption that the absorbance reached a limiting value which indicated that all of the iron was present in the form of the complex. Figs. 11, 12, and 13 contain the log ratio plots for the ammonia, hydrazine, and ethylenediamine complexes. Table 14 contains the apparent stability constants and combining ratios found.

Table 14. Apparent stability constants and combining ratios for Fe(II)-heptoxime-amine complexes

System	pK	n
Fe(II)-heptoxime-hydrazine	4.27	1.01
Fe(II)-heptoxime-ammonia	4.35	0.95
Fe(II)-heptoxime-ethylenediamine	5.67	1.11

Upon examination of the data given in Table 12, it can be seen that there is a marked spectral shift as the heptoxime concentration was raised above 5×10^{-4} M. The values measured at this concentration were assumed to correspond to the formation of a one to one complex with all the iron present in the form of the complex. Although this assumption was somewhat questionable, the calculations were carried out in order to gain some information on the stability of the complex.

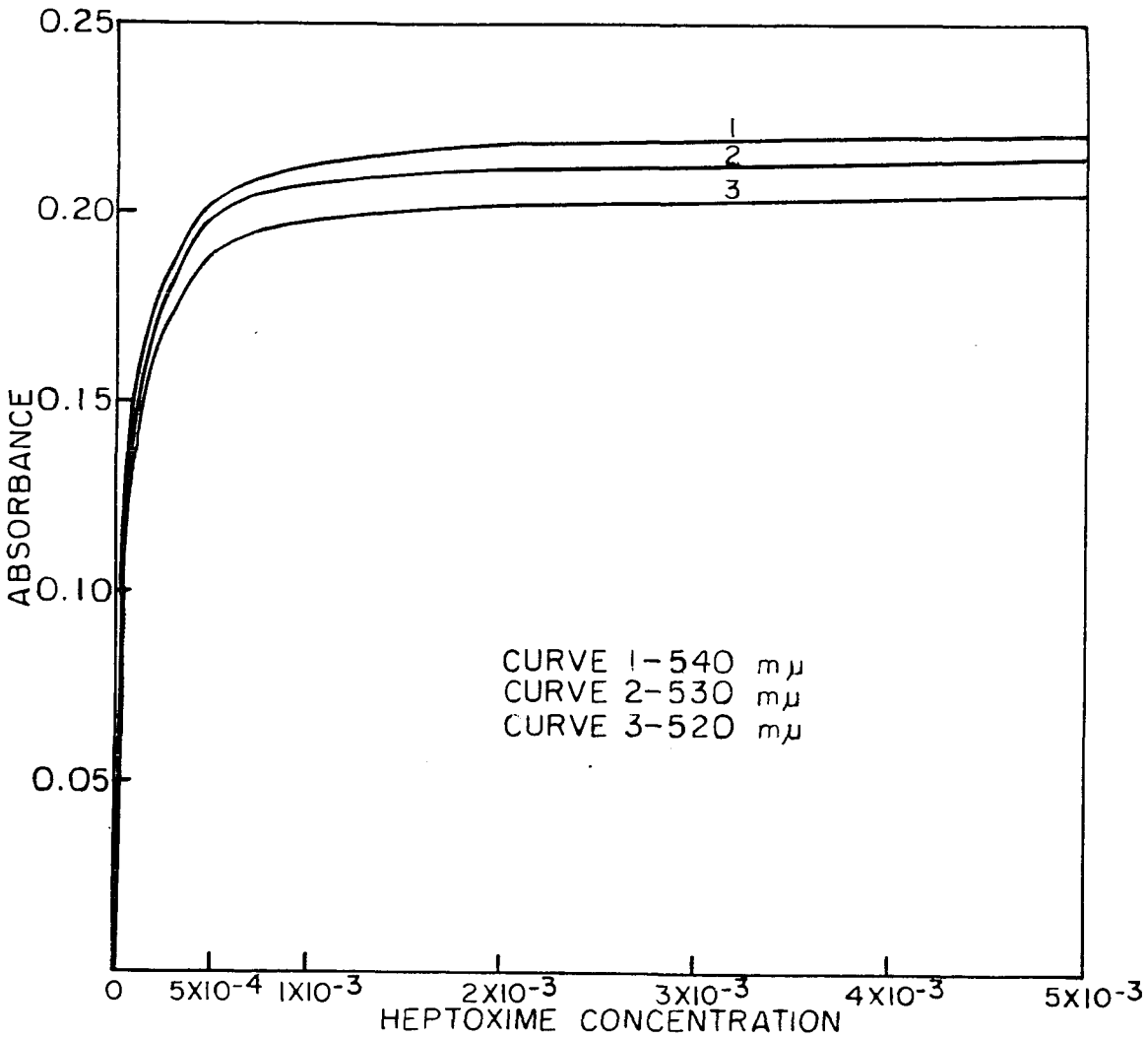


Fig. 10. Plot illustrating limiting absorbance for iron(II)-heptoxime-hydrazine system

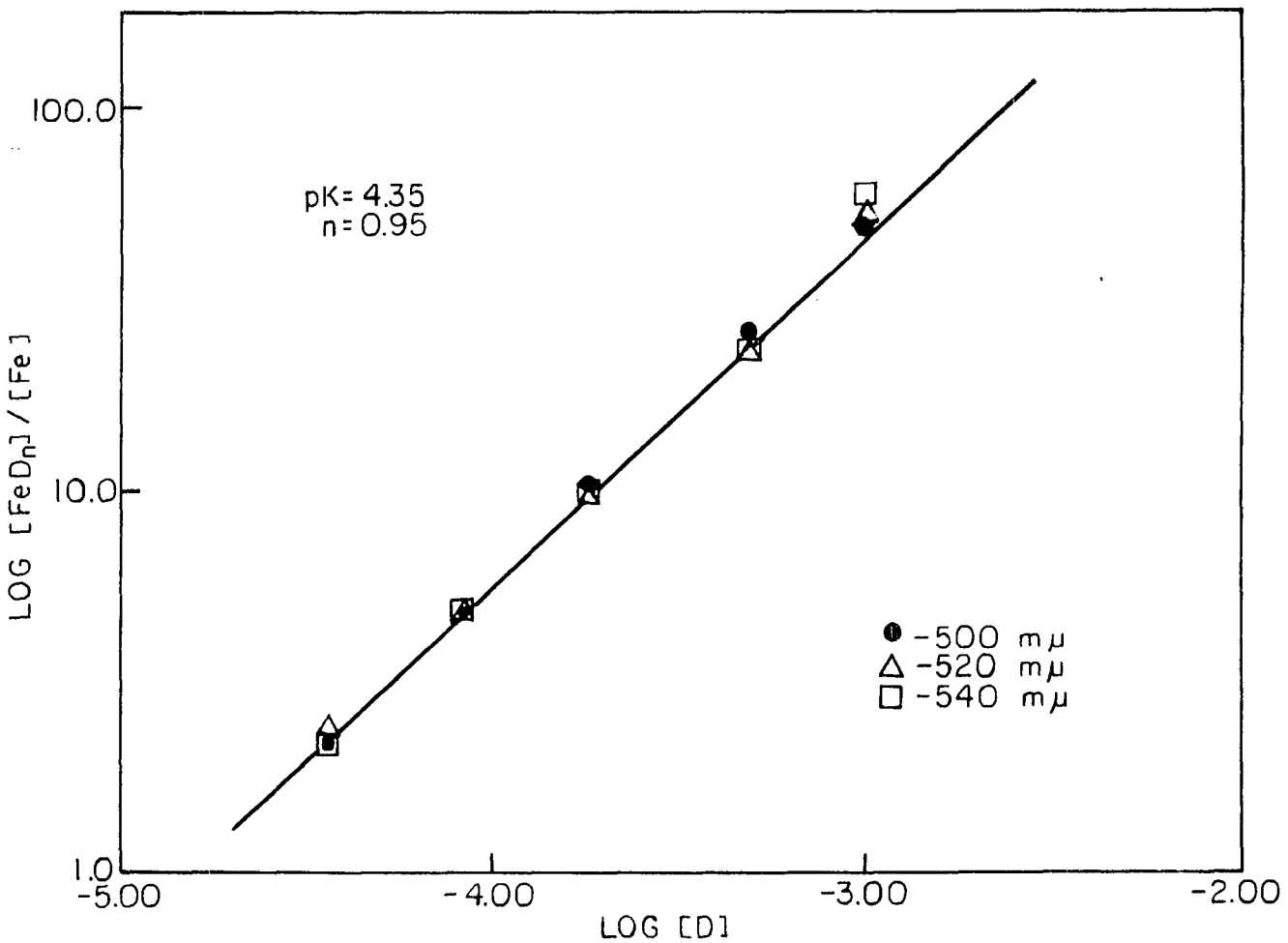


Fig. 11. Log ratio method for iron(II)-heptoxime-ammonia system

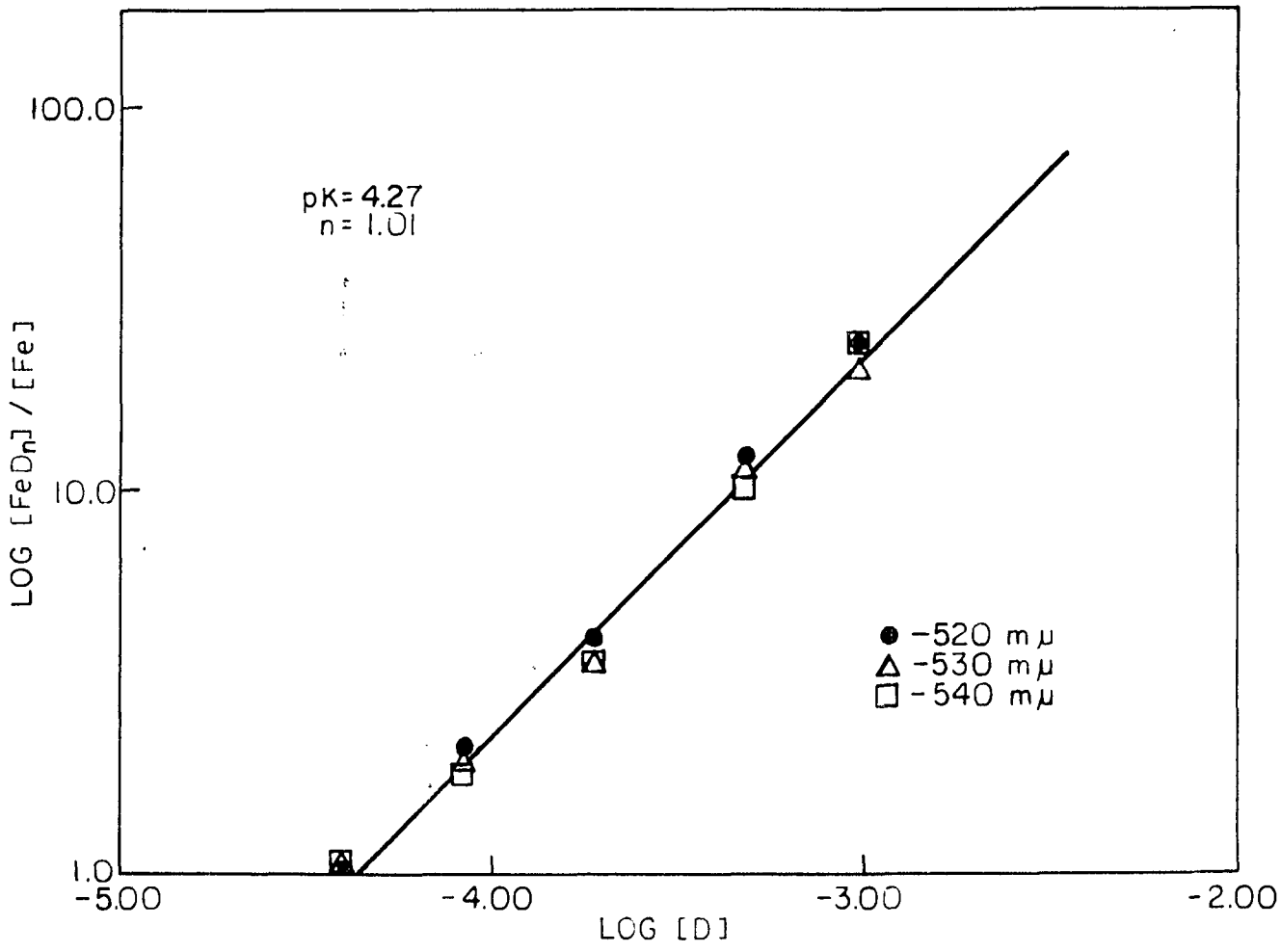


Fig. 12. Log ratio method for iron(II)-heptoxime-hydrazine system

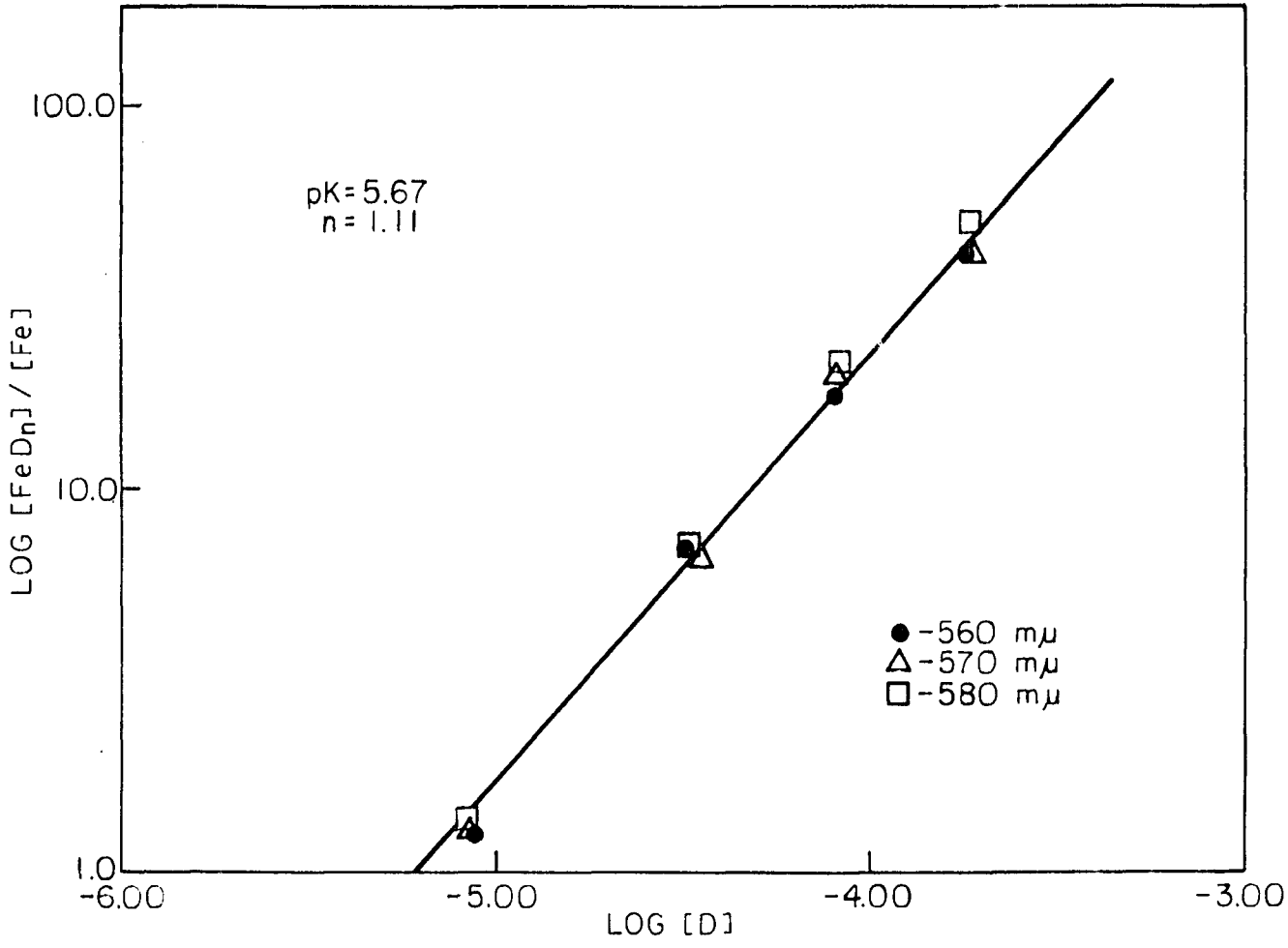


Fig. 13. Log ratio method for iron(II)-heptoxime-ethylenediamine system

The spectral shift undoubtedly indicates the formation of the two to one complex.

(b) Dimethylglyoxime. The Fe(II) complexes of dimethylglyoxime were studied in conjunction with ammonia, hydrazine, and ethylenediamine. Absorbance readings were made on each solution at wave lengths near the absorption maximum. The results with ammonia, hydrazine, and ethylenediamine are tabulated in Tables 15, 16, and 17, respectively. Figs. 14, 15, and 16 contain the log ratio plots for the ammonia, hydrazine, and ethylenediamine complexes. Table 18 summarizes the apparent stability constants and combining ratios found.

In the dimethylglyoxime-ethylenediamine system as in the case of the heptoxime-ethylenediamine system there was a spectral shift as the vic-dioxime concentration exceeded 5×10^{-4} M. The calculation was carried out as before to obtain some information on the stability of the complex even though it was not as accurate as could be desired.

(c) Nioxime. The Fe(II) complexes of nioxime were studied in conjunction with ammonia, hydroxylamine, and ethylenediamine. Absorbance readings were made on each solution at wave lengths near the absorption maximum. The results with ammonia, hydroxylamine, and ethylenediamine are tabulated in Tables 19, 20, and 21, respectively. Figs. 17, 18, and 19 contain the log ratio plots for the ammonia, hydroxylamine

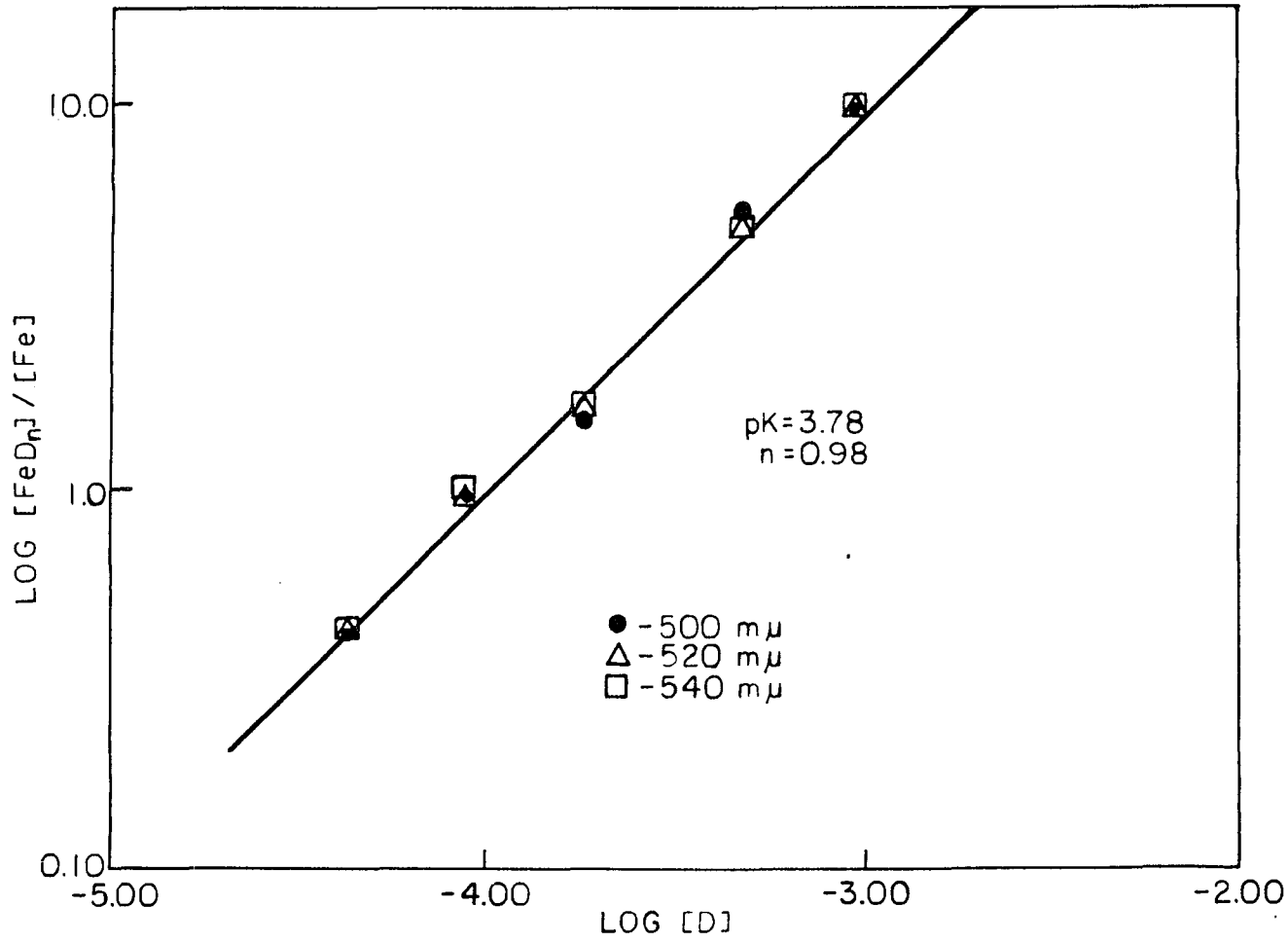


Fig. 14. Log ratio method for iron(II)-dimethylglyoxime-ammonia system

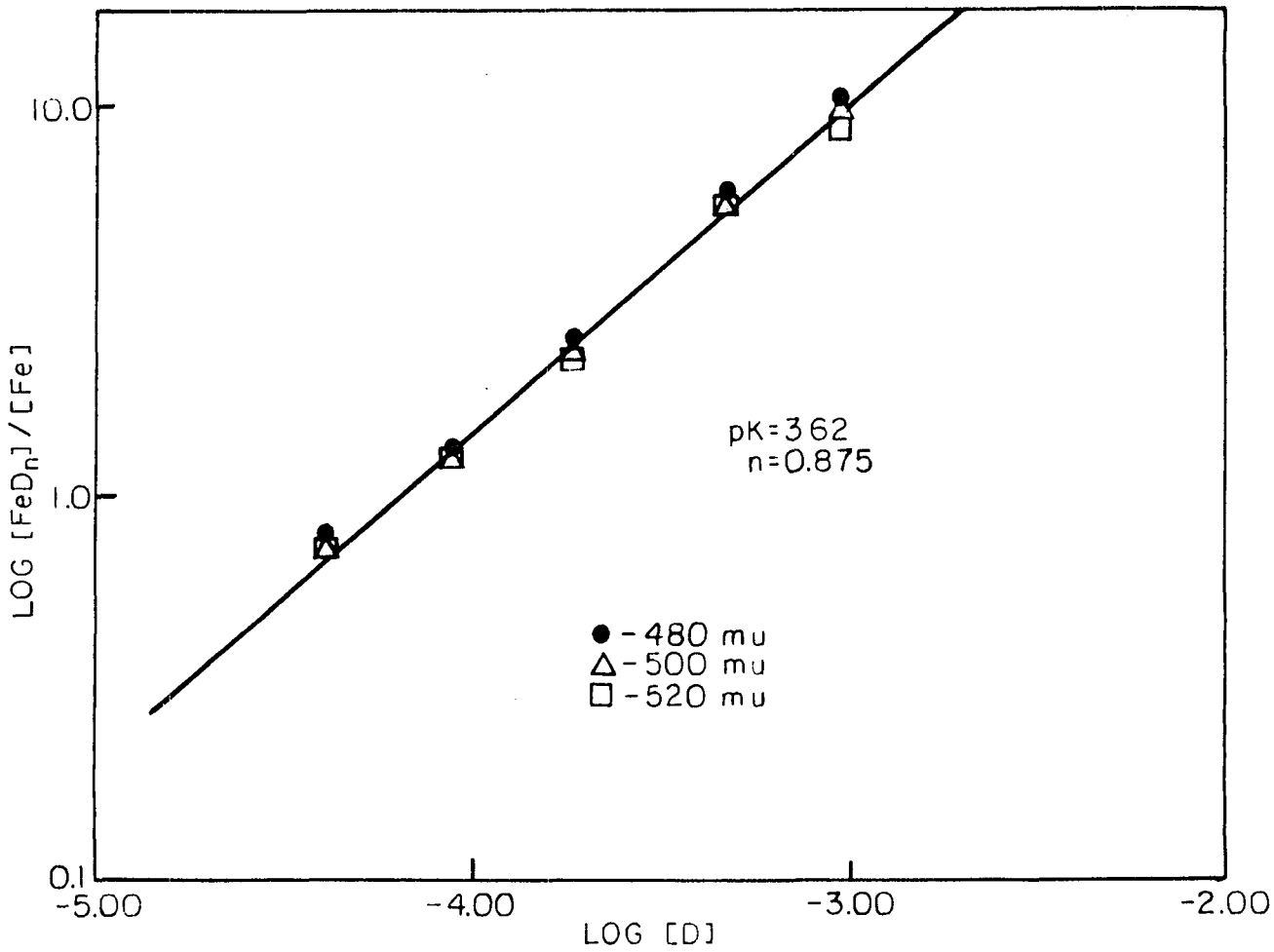


Fig. 15. Log ratio method for iron(II)-dimethylglyoxime-hydrazine system

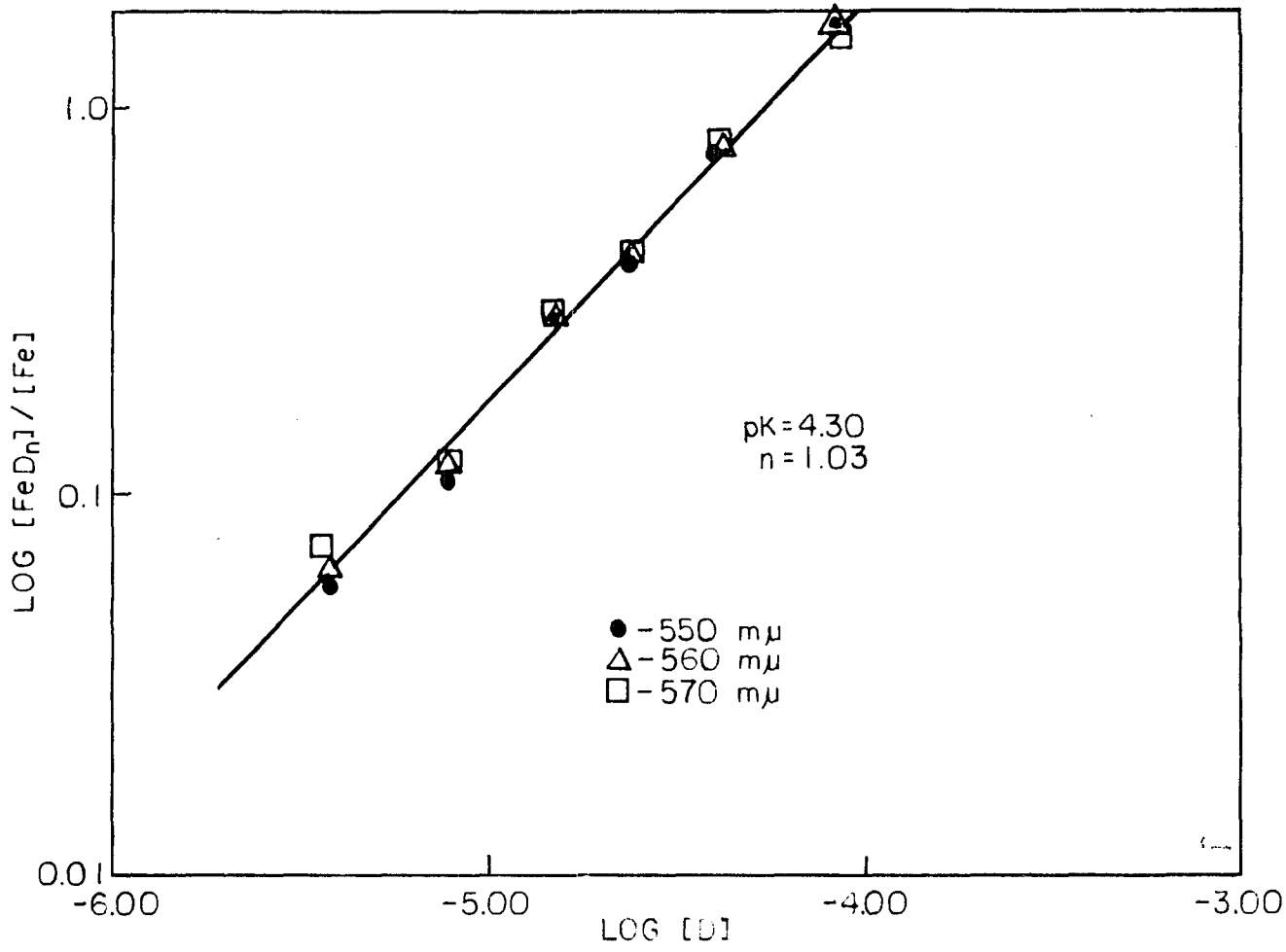


Fig. 16. Log ratio method for iron(II)-dimethylglyoxime-ethylenediamine system

Table 15. Log ratio method for Fe(II)-dimethylglyoxime-ammonia[a]

Concentration of dimethylglyoxime	A^{500}	A^{520}	A^{540}
5×10^{-5} M	0.050	0.053	0.048
5×10^{-5} M	0.051	0.054	0.049
5×10^{-5} M	0.048	0.052	0.047
1×10^{-4} M	0.081	0.087	0.079
1×10^{-4} M	0.082	0.084	0.079
1×10^{-4} M	0.081	0.084	0.079
2×10^{-4} M	0.102	0.107	0.097
2×10^{-4} M	0.104	0.108	0.098
2×10^{-4} M	0.101	0.108	0.097
5×10^{-4} M	0.141	0.144	0.134
5×10^{-4} M	0.141	0.145	0.134
5×10^{-4} M	0.139	0.142	0.131
1×10^{-3} M	0.151	0.157	0.145
1×10^{-3} M	0.152	0.158	0.146
1×10^{-3} M	0.153	0.158	0.146
2×10^{-3} M	0.160	0.167	0.155
2×10^{-3} M	0.160	0.167	0.156
2×10^{-3} M	0.159	0.167	0.154
5×10^{-3} M	0.168	0.175	0.161
5×10^{-3} M	0.167	0.174	0.161

[a]Absorbances determined after five hours

Table 16. Log ratio method for Fe(II)-dimethylglyoxime-hydrazine[a]

Concentration of dimethylglyoxime	A^{480}	A^{500}	A^{520}
5×10^{-5} M	0.057	0.056	0.055
5×10^{-5} M	0.058	0.056	0.056
5×10^{-5} M	0.057	0.055	0.056
1×10^{-4} M	0.074	0.073	0.072
1×10^{-4} M	0.074	0.073	0.073
1×10^{-4} M	0.077	0.076	0.075
2×10^{-4} M	0.094	0.092	0.092
2×10^{-4} M	0.092	0.091	0.093
2×10^{-4} M	0.092	0.092	0.091
5×10^{-4} M	0.112	0.112	0.114
5×10^{-4} M	0.111	0.112	0.113
5×10^{-4} M	0.114	0.113	0.113
1×10^{-3} M	0.117	0.118	0.117
1×10^{-3} M	0.119	0.119	0.120
1×10^{-3} M	0.121	0.120	0.120
2×10^{-3} M	0.124	0.125	0.127
2×10^{-3} M	0.123	0.125	0.126
2×10^{-3} M	0.124	0.125	0.126
5×10^{-3} M	0.130	0.137	0.132
5×10^{-3} M	0.129	0.136	0.132

[a]Absorbances determined after six hours

Table 17. Log ratio method for Fe(II)-dimethylglyoxime-ethylenediamine[a]

Concentration of dimethylglyoxime	A^{520}	A^{530}	A^{540}	A^{550}	A^{560}	A^{570}
5×10^{-6} M	0.004	0.006	0.007	0.008	0.009	0.009
5×10^{-6} M	0.004	0.005	0.007	0.008	0.008	0.009
1×10^{-5} M	0.008	0.010	0.012	0.013	0.015	0.015
1×10^{-5} M	0.010	0.012	0.012	0.014	0.014	0.015
2×10^{-5} M	0.021	0.027	0.031	0.032	0.031	0.030
2×10^{-5} M	0.021	0.025	0.030	0.031	0.034	0.032
3×10^{-5} M	0.029	0.033	0.038	0.042	0.043	0.041
3×10^{-5} M	0.028	0.035	0.039	0.040	0.041	0.039
5×10^{-5} M	0.048	0.054	0.059	0.062	0.063	0.062
5×10^{-5} M	0.047	0.054	0.059	0.060	0.063	0.062
1×10^{-4} M	0.070	0.077	0.084	0.087	0.089	0.088
1×10^{-4} M	0.072	0.078	0.086	0.089	0.091	0.088
2×10^{-4} M	0.095	0.106	0.113	0.115	0.118	0.115
2×10^{-4} M	0.092	0.102	0.110	0.114	0.117	0.116
5×10^{-4} M	0.115	0.126	0.135	0.141	0.145	0.141
5×10^{-4} M	0.116	0.128	0.137	0.143	0.146	0.143
1×10^{-3} M	0.125	0.133	0.134	0.137	0.136	0.130
1×10^{-3} M	0.124	0.130	0.136	0.138	0.137	0.130
2×10^{-3} M	0.130	0.133	0.135	0.133	0.129	0.117
2×10^{-3} M	0.129	0.134	0.133	0.130	0.125	0.113
5×10^{-3} M	0.138	0.138	0.134	0.127	0.118	0.105
5×10^{-3} M	0.138	0.137	0.136	0.128	0.120	0.106

[a]Absorbances determined after ten hours

Table 18. Apparent stability constants and combining ratios for Fe(II)-dimethylglyoxime-amine complexes

System	pK	n
Fe(II)-dimethylglyoxime-ammonia	3.78	0.98
Fe(II)-dimethylglyoxime-hydrazine	3.62	0.88
Fe(II)-dimethylglyoxime-ethylenediamine	4.30	1.03

Table 19. Log ratio method for Fe(II)-nioxime-ammonia[a]

Concentration of nioxime	A^{500}	A^{520}	A^{540}
1×10^{-4} M	0.114	0.120	0.114
1×10^{-4} M	0.110	0.121	0.117
1×10^{-4} M	0.111	0.118	0.117
2×10^{-4} M	0.150	0.166	0.162
2×10^{-4} M	0.150	0.166	0.161
2×10^{-4} M	0.151	0.167	0.160
5×10^{-4} M	0.165	0.180	0.178
5×10^{-4} M	0.165	0.182	0.178
5×10^{-4} M	0.165	0.177	0.175
1×10^{-3} M	0.166	0.182	0.179
1×10^{-3} M	0.168	0.182	0.179
1×10^{-3} M	0.165	0.181	0.180
2×10^{-3} M	0.167	0.183	0.182
2×10^{-3} M	0.168	0.182	0.179
2×10^{-3} M	0.167	0.183	0.180
5×10^{-3} M	0.168	0.183	0.181
5×10^{-3} M	0.166	0.182	0.179
5×10^{-3} M	0.169	0.184	0.182

[a]Absorbances determined after five hours

Table 20. Log ratio method for Fe(II)-nioxime-hydroxylamine[a]

Concentration of nioxime	A^{500}	A^{520}	A^{540}
1×10^{-4} M	0.121	0.138	0.142
1×10^{-4} M	0.122	0.138	0.142
1×10^{-4} M	0.119	0.137	0.137
2×10^{-4} M	0.139	0.166	0.158
2×10^{-4} M	0.138	0.162	0.157
2×10^{-4} M	0.141	0.163	0.162
5×10^{-4} M	0.156	0.182	0.180
5×10^{-4} M	0.156	0.183	0.181
5×10^{-4} M	0.153	0.181	0.180
1×10^{-3} M	0.159	0.186	0.185
1×10^{-3} M	0.158	0.188	0.184
1×10^{-3} M	0.159	0.188	0.183
2×10^{-3} M	0.163	0.190	0.187
2×10^{-3} M	0.163	0.191	0.188
2×10^{-3} M	0.163	0.191	0.188
5×10^{-3} M	0.165	0.193	0.190
5×10^{-3} M	0.164	0.192	0.190
5×10^{-3} M	0.165	0.194	0.191

[a]Absorbances determined after five hours

Table 21. Log ratio method for Fe(II)-nioxime-ethylenediamine[a]

Concentration of nioxime	A^{500}	A^{520}	A^{540}	A^{560}	A^{580}	A^{600}
2.5×10^{-6} M	0.003	0.004	0.004	0.004	0.005	0.003
2.5×10^{-6} M	0.003	0.003	0.004	0.005	0.005	0.003
5×10^{-6} M	0.007	0.008	0.008	0.010	0.011	0.008
5×10^{-6} M	0.007	0.007	0.008	0.010	0.011	0.007
1×10^{-5} M	0.013	0.015	0.016	0.019	0.020	0.017
1×10^{-5} M	0.014	0.015	0.015	0.018	0.019	0.016

[a]Absorbances determined after five hours

Table 21. (Continued)

Concentration of nioxime	A^{500}	A^{520}	A^{540}	A^{560}	A^{580}	A^{600}
2×10^{-5} M	0.029	0.033	0.035	0.037	0.041	0.039
2×10^{-5} M	0.027	0.031	0.035	0.036	0.039	0.037
5×10^{-5} M	0.055	0.065	0.067	0.071	0.077	0.072
5×10^{-5} M	0.055	0.065	0.068	0.072	0.073	0.069
1×10^{-4} M	0.072	0.087	0.118	0.173	0.196	0.173
1×10^{-4} M	0.069	0.083	0.116	0.171	0.198	0.175
2×10^{-4} M	0.094	0.115	0.151	0.175	0.174	0.150
2×10^{-4} M	0.093	0.113	0.148	0.174	0.175	0.153
5×10^{-4} M	0.120	0.134	0.164	0.173	0.154	0.110
5×10^{-4} M	0.117	0.130	0.161	0.173	0.157	0.108
1×10^{-3} M	0.122	0.134	0.164	0.175	0.151	0.094
1×10^{-3} M	0.120	0.135	0.164	0.173	0.149	0.091
2×10^{-3} M	0.121	0.135	0.165	0.175	0.147	0.090
2×10^{-3} M	0.121	0.135	0.164	0.174	0.148	0.089

and ethylenediamine complexes. Table 22 summarizes the apparent stability constants and combining ratios found. The situation found in the case of the nioxime-ethylenediamine system was analogous to the two preceding (ethylenediamine) cases and was treated in the same manner.

(d) 2,2'-pyridildioxime. The Fe(II) complexes of 2,2'-pyridildioxime were studied in conjunction with ammonia, pyridine, hydrazine, and ethylenediamine. Absorbance readings

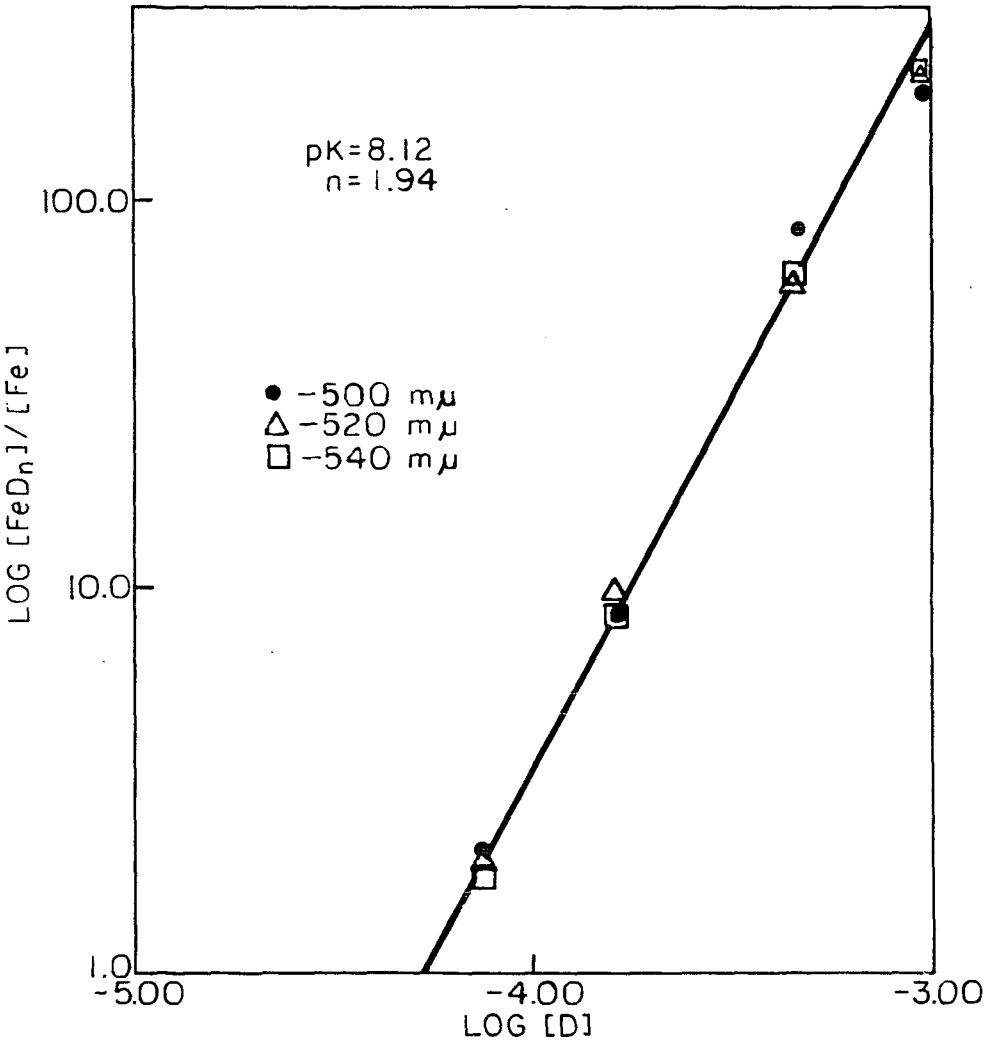


Fig. 17. Log ratio method for iron(II)-nioxime-ammonia system

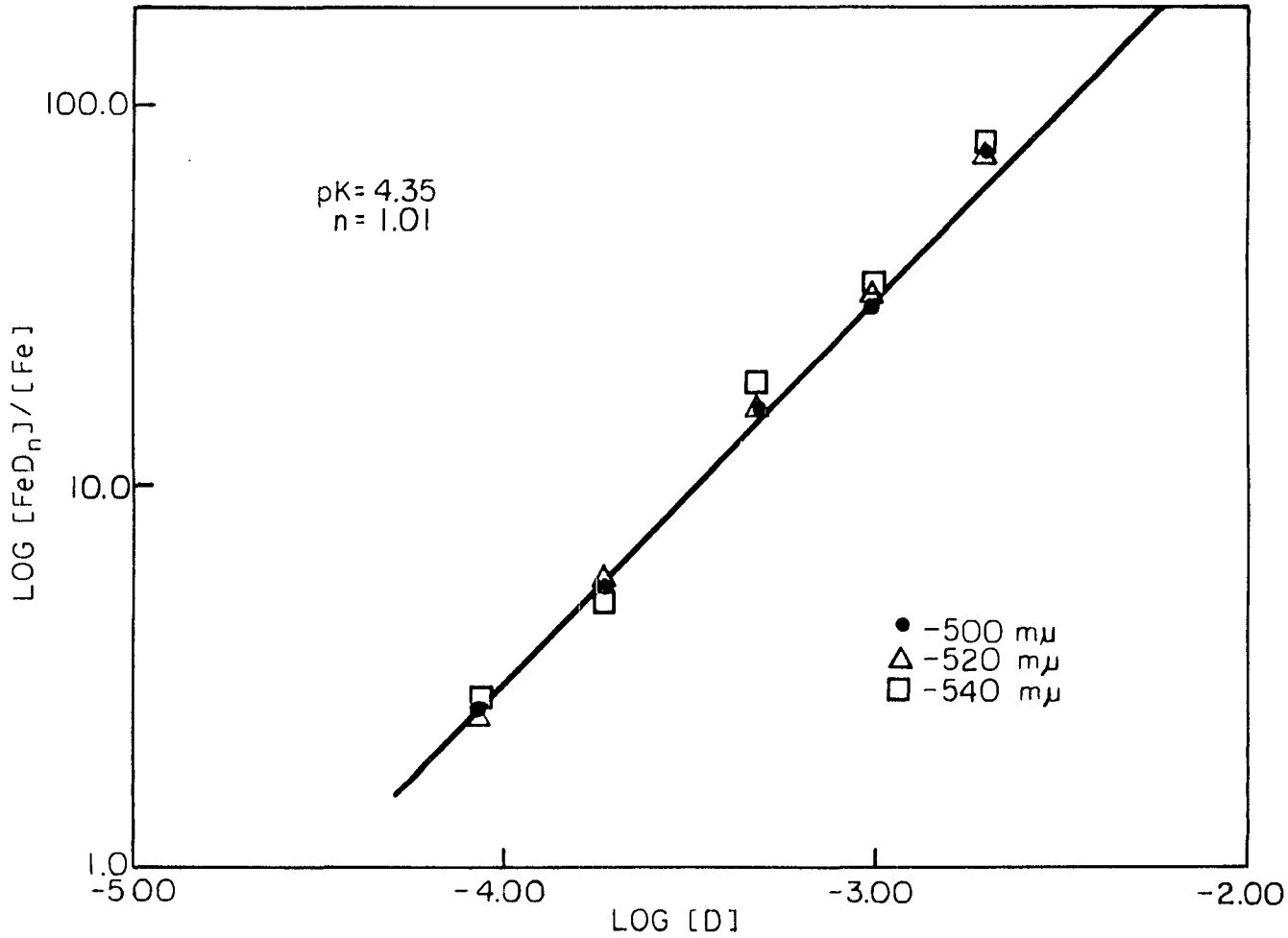


Fig. 18. Log ratio method for iron(II)-nioxime-hydroxylamine system

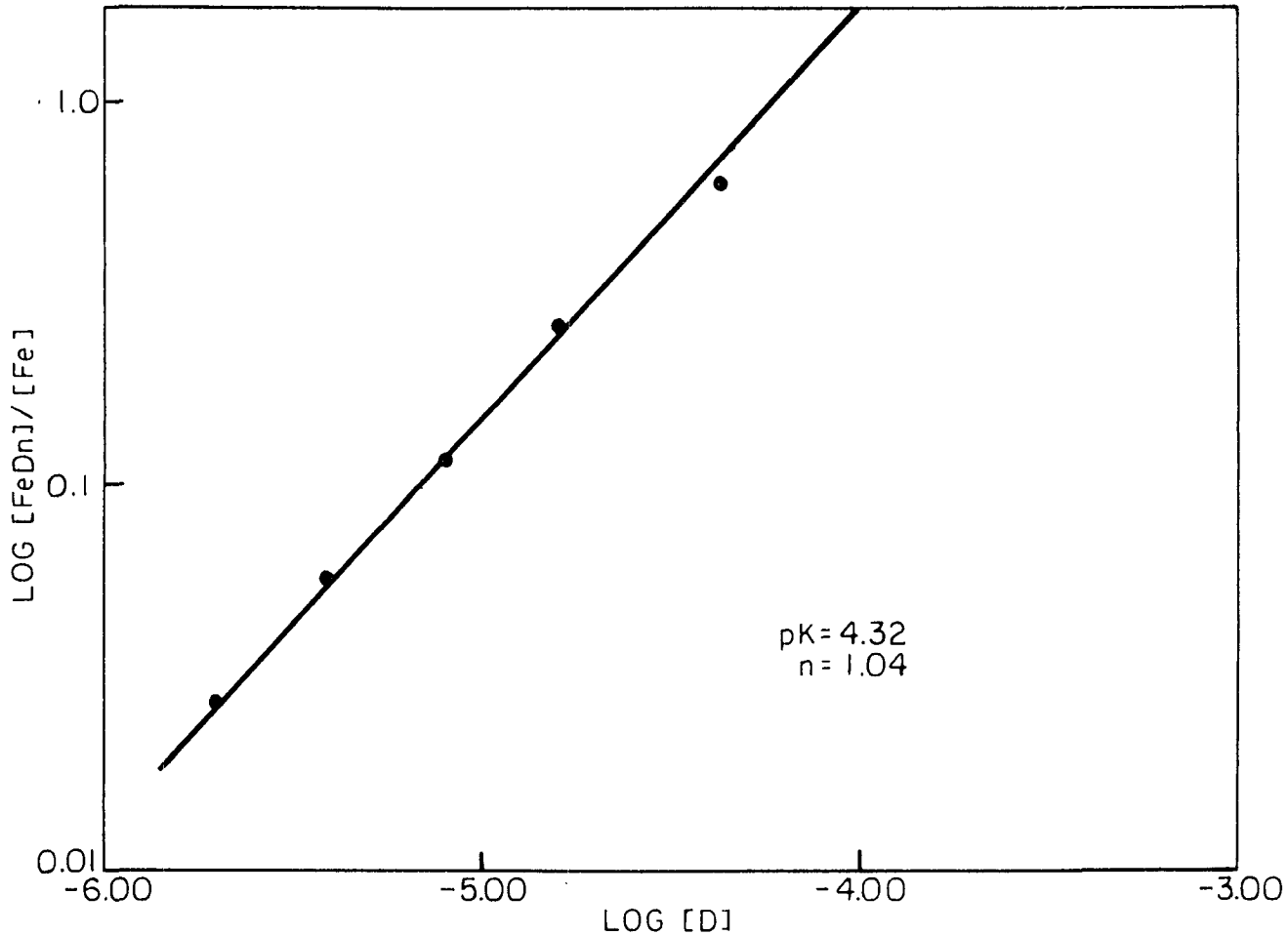


Fig. 19. Log ratio method for iron(II)-nioxime-ethylenediamine system

Table 22. Apparent stability constants and combining ratios for Fe(II)-nioxime-amine complexes

System	pK	n
Fe(II)-nioxime-ammonia	8.12	1.94
Fe(II)-nioxime-hydroxylamine	4.35	1.01
Fe(II)-nioxime-ethylenediamine	4.32	1.04

were made on each solution at wave lengths near the absorption maximum. The results with ammonia, pyridine, hydrazine, and ethylenediamine are tabulated in Tables 23, 24, 25, and 26, respectively. Figs. 20, 21, 22, and 23 contain the log ratio plots for the various complexes. Table 27 summarizes the apparent stability constants and combining ratios found.

Throughout the study of the apparent stability constants of the four vic-dioximes a change in the absorption spectrum of the complex was noticed at very high vic-dioxime concentrations. The Fe(II)-2,2'-pyridildioxime-ammonia system is used as an example here. The fraction of iron complexed in the solution having a 2,2'-pyridildioxime concentration of 5×10^{-5} M was calculated. The absorbance values of this solution were extrapolated to a 100 per cent iron complex. This calculated spectrum is shown in Fig. 24 with the actual spectrum of the solution measured with the 2,2'-pyridildioxime concentration at 2×10^{-3} M. It is evident that the spectra

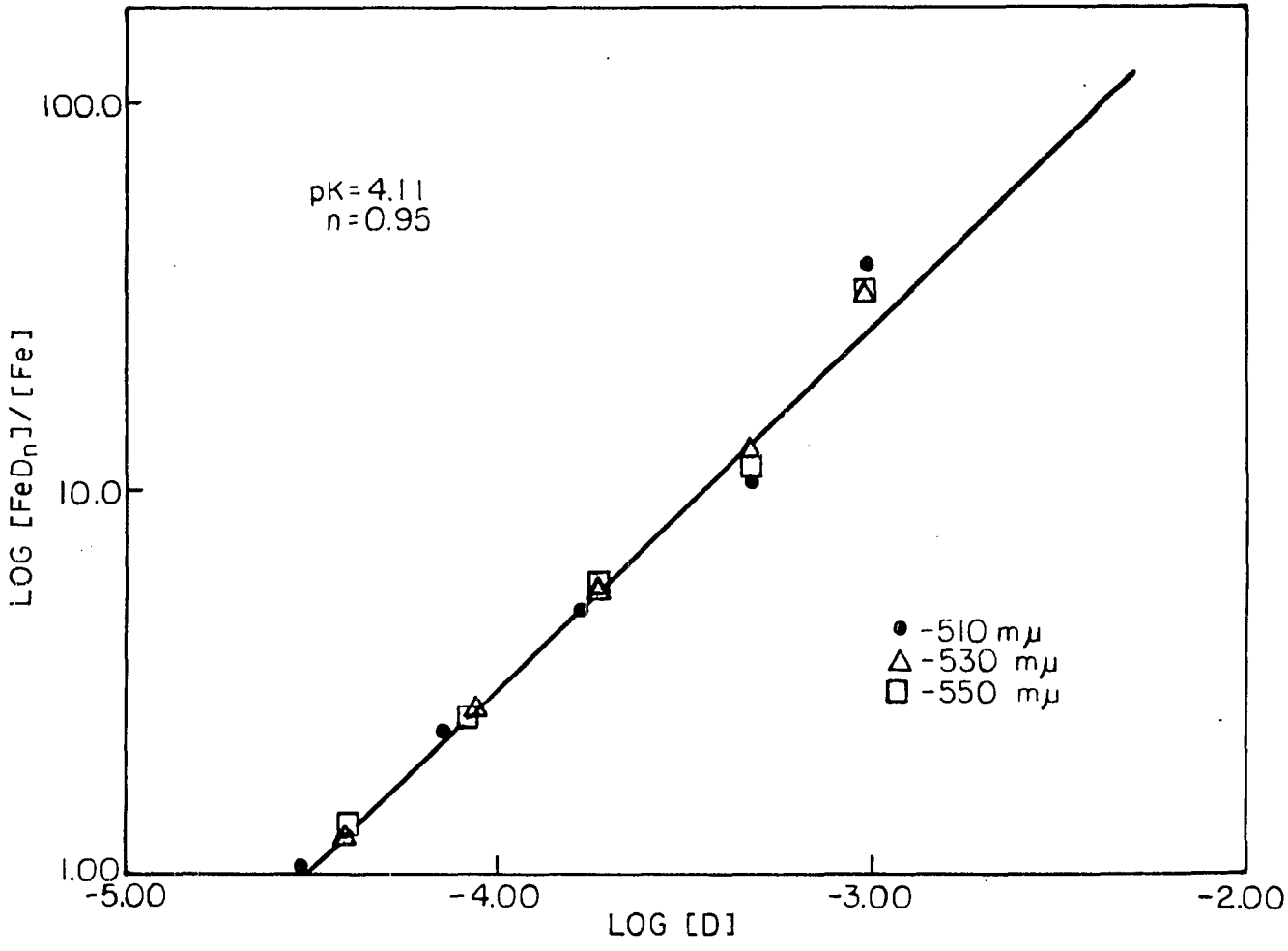


Fig. 20. Log ratio method for iron(II)-2,2'-pyridildioxime-ammonia system

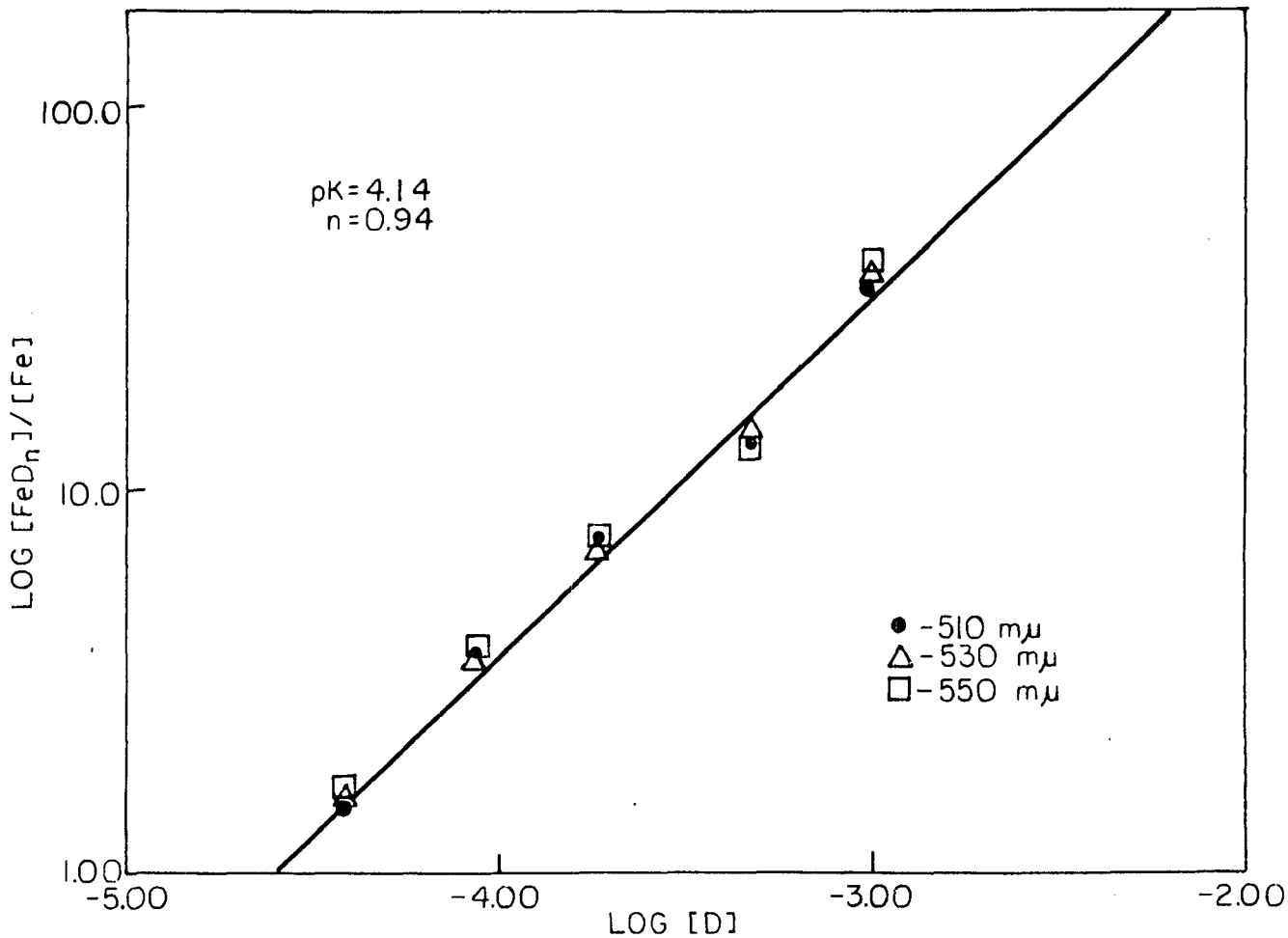


Fig. 21. Log ratio method for iron(II)-2,2'-pyridildioxime-pyridine system

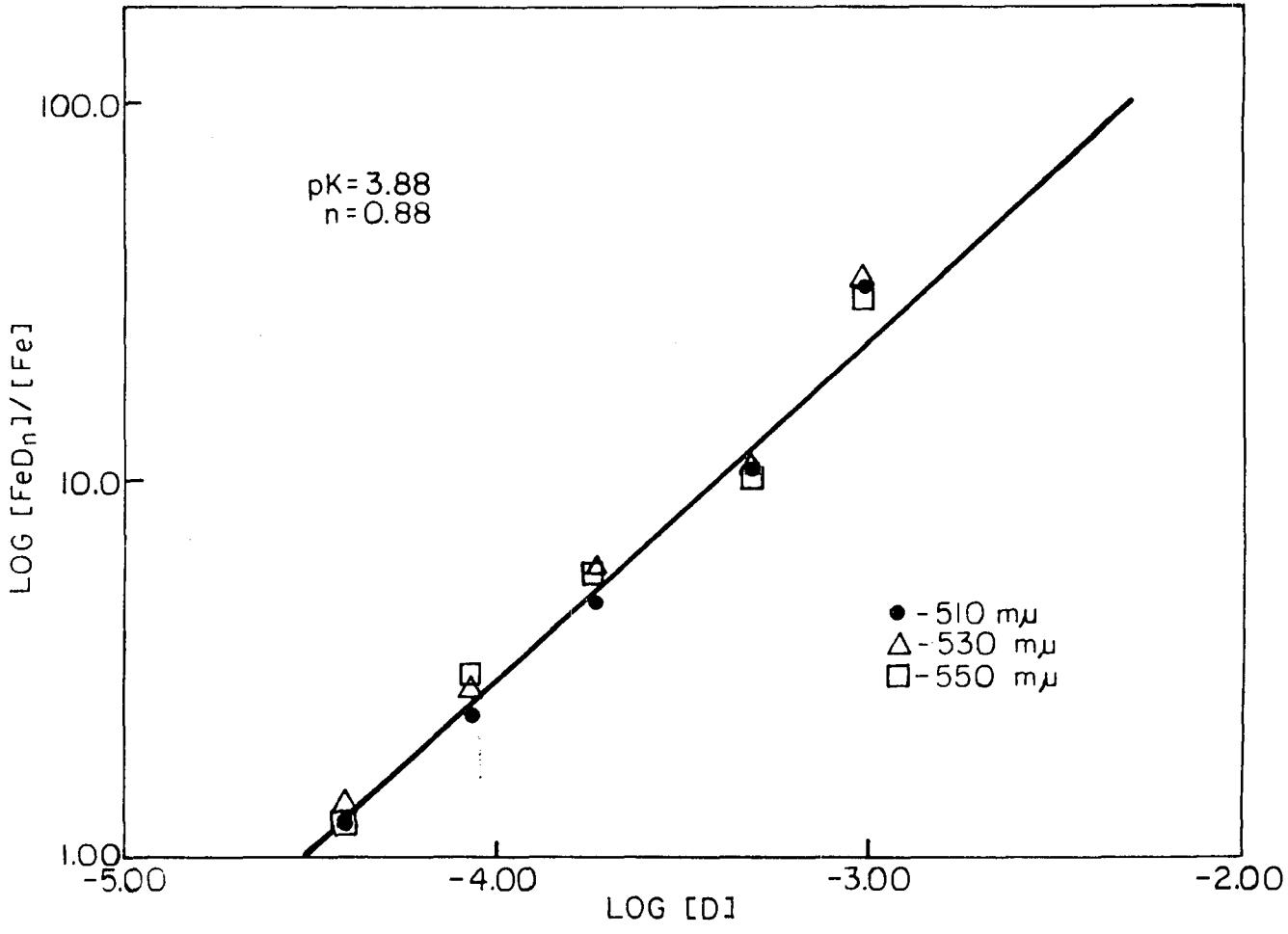


Fig. 22. Log ratio method for iron(II)-2,2'-pyridildioxime-hydrazine system

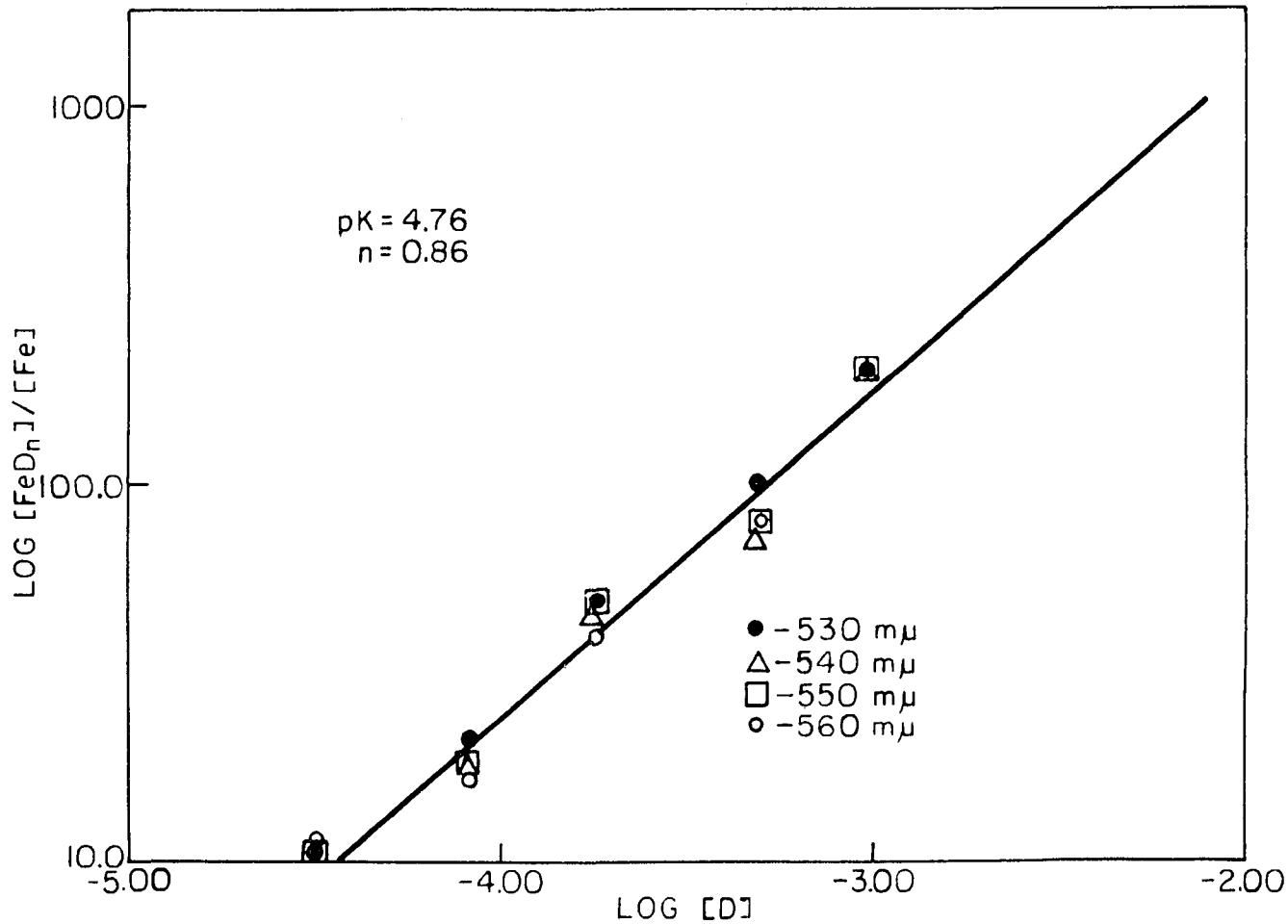


Fig. 23. Log ratio method for iron(II)-2,2'-pyridildioxime-ethylenediamine system

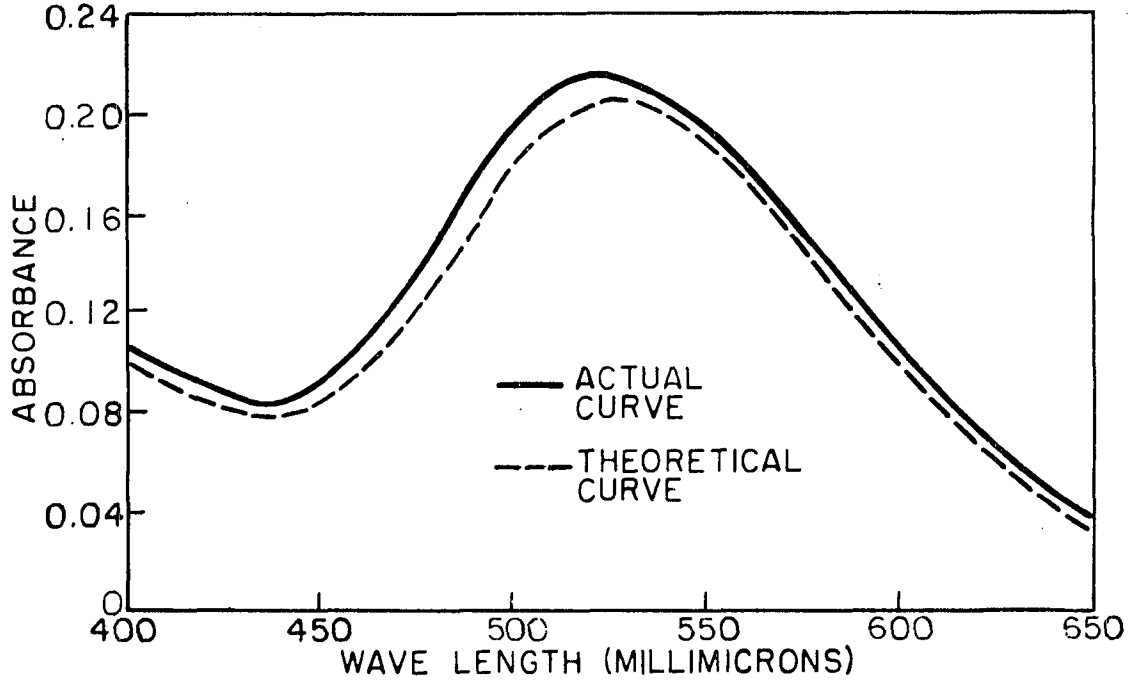


Fig. 24. Absorption curves illustrating the changes in the iron(II)-2,2'-pyridildioxime-ammonia spectrum with increasing 2,2'-pyridildioxime concentration

Table 23. Log ratio method for Fe(II)-2,2'pyridildioxime-ammonia[a]

Concentration of 2,2'-pyridildioxime	A^{510}	A^{530}	A^{550}
5×10^{-5} M	0.120	0.130	0.118
5×10^{-5} M	0.112	0.123	0.114
5×10^{-5} M	0.117	0.127	0.113
1×10^{-4} M	0.156	0.165	0.148
1×10^{-4} M	0.155	0.165	0.148
1×10^{-4} M	0.157	0.166	0.147
2×10^{-4} M	0.190	0.190	0.174
2×10^{-4} M	0.184	0.193	0.171
2×10^{-4} M	0.186	0.193	0.175
5×10^{-4} M	0.208	0.210	0.188
5×10^{-4} M	0.204	0.208	0.186
5×10^{-4} M	0.207	0.210	0.187
1×10^{-3} M	0.222	0.222	0.198
1×10^{-3} M	0.218	0.220	0.199
1×10^{-3} M	0.219	0.220	0.198
2×10^{-3} M	0.223	0.225	0.202
2×10^{-3} M	0.222	0.226	0.202
2×10^{-3} M	0.224	0.227	0.204
5×10^{-3} M	0.225	0.227	0.204
5×10^{-3} M	0.224	0.227	0.204

[a]Absorbances determined after ten hours

Table 24. Log ratio method for Fe(II)-2,2'-pyridildioxime-pyridine[a]

Concentration of 2,2'-pyridildioxime	A^{510}	A^{530}	A^{550}
5×10^{-5} M	0.117	0.137	0.125
5×10^{-5} M	0.119	0.140	0.127
5×10^{-5} M	0.120	0.139	0.128
1×10^{-4} M	0.155	0.177	0.160
1×10^{-4} M	0.156	0.176	0.161
1×10^{-4} M	0.157	0.177	0.166
2×10^{-4} M	0.172	0.194	0.179
2×10^{-4} M	0.174	0.195	0.179
2×10^{-4} M	0.177	0.198	0.182
5×10^{-4} M	0.179	0.203	0.186
5×10^{-4} M	0.180	0.202	0.187
5×10^{-4} M	0.180	0.204	0.187
1×10^{-3} M	0.192	0.216	0.200
1×10^{-3} M	0.192	0.215	0.201
1×10^{-3} M	0.193	0.216	0.200
2×10^{-3} M	0.195	0.220	0.203
2×10^{-3} M	0.197	0.220	0.204
2×10^{-3} M	0.197	0.220	0.204
5×10^{-3} M	0.198	0.222	0.205
5×10^{-3} M	0.199	0.221	0.205

[a]Absorbances determined after eleven hours

Table 25. Log ratio method for Fe(II)-2,2'-pyridildioxime-hydrazine[a]

Concentration of 2,2'-pyridildioxime	A^{510}	A^{530}	A^{550}
5×10^{-5} M	0.115	0.124	0.104
5×10^{-5} M	0.111	0.121	0.100

[a]Absorbances determined after eleven hours

Table 25. (Continued)

Concentration of 2,2'-pyridildioxime	A^{510}	A^{530}	A^{550}
5×10^{-5} M	0.112	0.123	0.103
1×10^{-4} M	0.147	0.157	0.143
1×10^{-4} M	0.141	0.152	0.135
1×10^{-4} M	0.144	0.156	0.140
2×10^{-4} M	0.165	0.176	0.155
2×10^{-4} M	0.170	0.183	0.160
2×10^{-4} M	0.168	0.180	0.157
5×10^{-4} M	0.185	0.190	0.170
5×10^{-4} M	0.187	0.190	0.168
5×10^{-4} M	0.187	0.191	0.168
1×10^{-3} M	0.197	0.202	0.180
1×10^{-3} M	0.199	0.203	0.180
1×10^{-3} M	0.199	0.204	0.181
2×10^{-3} M	0.200	0.206	0.184
2×10^{-3} M	0.203	0.207	0.185
2×10^{-3} M	0.203	0.207	0.184
5×10^{-3} M	0.204	0.209	0.186
5×10^{-3} M	0.203	0.209	0.185

Table 26. Log ratio method for Fe(II)-2,2'-pyridildioxime-ethylenediamine[a]

Concentration of 2,2'-pyridildioxime	A^{530}	A^{540}	A^{550}	A^{560}
5×10^{-5} M	0.181	0.211	0.228	0.220
5×10^{-5} M	0.176	0.206	0.222	0.220
5×10^{-5} M	0.179	0.209	0.225	0.220

[a]Absorbances determined after twelve hours

Table 26. (Continued)

Concentration of 2,2'-pyridildioxime	A^{530}	A^{540}	A^{550}	A^{560}
$1x10^{-4}$ M	0.186	0.218	0.234	0.226
$1x10^{-4}$ M	0.187	0.219	0.234	0.227
$1x10^{-4}$ M	0.187	0.219	0.234	0.227
$2x10^{-4}$ M	0.191	0.227	0.242	0.236
$2x10^{-4}$ M	0.192	0.225	0.241	0.234
$2x10^{-4}$ M	0.192	0.226	0.242	0.236
$5x10^{-4}$ M	0.193	0.228	0.244	0.238
$5x10^{-4}$ M	0.195	0.228	0.244	0.239
$5x10^{-4}$ M	0.194	0.228	0.244	0.238
$1x10^{-3}$ M	0.194	0.229	0.245	0.239
$1x10^{-3}$ M	0.196	0.230	0.246	0.240
$1x10^{-3}$ M	0.195	0.230	0.246	0.240
$2x10^{-3}$ M	0.195	0.230	0.247	0.241
$2x10^{-3}$ M	0.196	0.231	0.247	0.242
$2x10^{-3}$ M	0.196	0.231	0.247	0.240

Table 27. Apparent stability constants and combining ratios for Fe(II)-2,2'-pyridildioxime-amine complexes

System	pK	n
Fe(II)-2,2'-pyridildioxime-ammonia	4.11	0.95
Fe(II)-2,2'-pyridildioxime-pyridine	4.14	0.94
Fe(II)-2,2'-pyridildioxime-hydrazine	3.88	0.88
Fe(II)-2,2'-pyridildioxime-ethylenediamine	4.76	0.86

are not identical either in absorption maxima or shape. This effect was present in varying degrees in all systems studied.

VI. DETERMINATION OF THE IONIC CHARGE OF SEVERAL IRON(II)-VIC-DIOXIME-AMINE COMPLEXES

A. Materials and Apparatus

All solutions used in this study were identical to those described in Section V-A. The cell which was used is shown in Fig. 25. It consisted of two chambers separated by a sintered glass plug. On one side of the plug an agar gel was formed to reduce diffusion of the solutions in the two chambers. The potassium chloride solution was prepared by adding Mallinckrodt Analytical Reagent grade potassium chloride to water until no more would dissolve. The electromotive force was supplied by six dry cells. Two groups of three cells each were connected in series and the two groups themselves were connected in parallel. This arrangement furnished 4.5 volts and sufficient current to perform the desired electrolysis.

B. Experimental Procedure

The purpose of this study was to determine the nature of the ionic charge, if any, of a number of the Fe(II)-vic-dioxime-amine complexes. No attempt was made to make quantitative measurements since qualitative information was sufficient to give the desired facts. In addition, quanti-

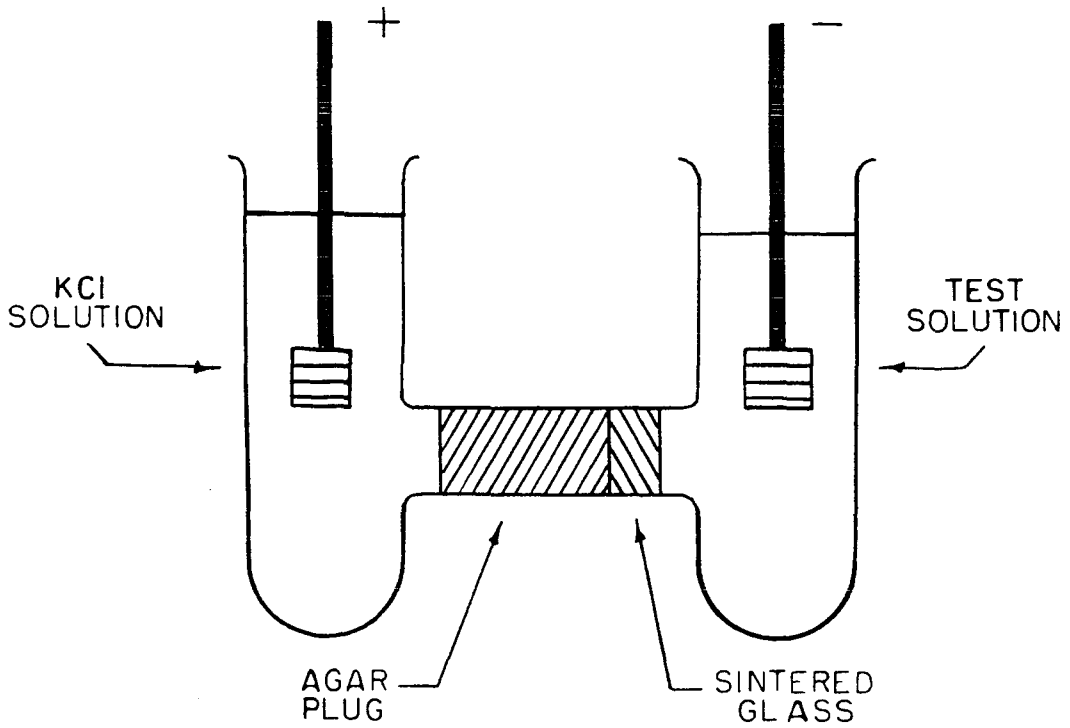


Fig. 25. Cell used in migration study

tative measurements would have been of dubious value due to the presence of two or more complexes in the system.

The solutions of the complexes were prepared in the following manner. Five ml. of carbonate buffer, 5 ml. of the desired 0.1 M amine solution, and 0.1 g. of sodium dithionite were placed in a 100 ml. volumetric flask. The mixture was diluted to approximately 40 ml. The desired amount of $1x10^{-2}$ M vic-dioxime solution and 4 ml. of $1x10^{-3}$ M Fe(II) chloride solution were then added and the mixture diluted to volume. This solution was placed in the electrolytic cell after standing six hours to allow the system to reach equilibrium. The current was adjusted to 20 ma. and the electrolysis continued for ninety minutes. The current was then turned off and the agar plug carefully removed. The plug was then placed in 20 ml. of water to which 1 ml. of carbonate buffer had been added. This mixture was stirred until the agar was evenly suspended throughout. A portion was then placed in a cuvette and the absorbance immediately determined with the Beckman model B spectrophotometer at a wave length of 530 millimicrons. The blank used was prepared in the same manner as the test runs except that no vic-dioxime was added.

C. Experimental Results

1. Nioxime

Four amines (ammonia, hydroxylamine, hydrazine, and ethylenediamine) were studied in conjunction with nioxime.

Two levels of nioxime concentration were used in conjunction with each amine. One run was made with a $2x10^{-4}$ M nioxime concentration and a similar run was made with the nioxime concentration at $5x10^{-3}$ M. The results of this study, shown in Table 28, are expressed in terms of the absorbance measured.

Table 28. Ion migration studies with nioxime complexes

Concentration of nioxime	Amine used	A^{530}
$2x10^{-4}$ M	Ammonia	0.008
$5x10^{-3}$ M	Ammonia	0.018
$2x10^{-4}$ M	Hydrazine	0.001
$5x10^{-3}$ M	Hydrazine	0.003
$2x10^{-4}$ M	Ethylenediamine	0.004
$5x10^{-3}$ M	Ethylenediamine	0.009
$2x10^{-4}$ M	Hydroxylamine	0.000
$5x10^{-3}$ M	Hydroxylamine	0.003

2. 2,2'-pyridildioxime

2,2'-pyridildioxime was studied in conjunction with hydroxylamine, pyridine, ethylenediamine, ammonia, and hydrazine. Two levels of dioxime concentration were used with

each amine. The results expressed in terms of absorbance are found in Table 29.

In several cases the solutions prepared were subjected to electrolysis in the reverse direction by placing the anode in the cell with the test solution. No migration of color into the agar plug toward the cathode was observed.

Table 29. Ion migration studies with 2,2'-pyridildioxime complexes

Concentration of 2,2'-pyridildioxime	Amine used	A^{530}
2×10^{-4} M	Ammonia	0.007
5×10^{-3} M	Ammonia	0.013
2×10^{-4} M	Hydroxylamine	0.003
5×10^{-3} M	Hydroxylamine	0.009
2×10^{-4} M	Ethylenediamine	0.000
5×10^{-3} M	Ethylenediamine	0.002
2×10^{-4} M	Hydrazine	0.002
5×10^{-3} M	Hydrazine	0.007
2×10^{-4} M	Pyridine	0.003
5×10^{-3} M	Pyridine	0.007

3. Discussion

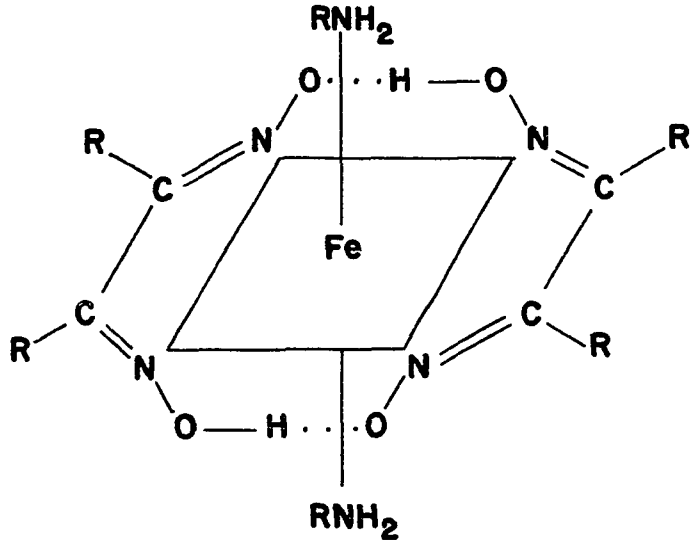
Upon examination of the results appearing in Tables 28 and 29 it is evident that there was indeed a negatively charged, colored species present. This is in accord with the findings of Matthews (23) and the prediction of Feigl and Suter (11). It was also observed that the amount of negatively charged species was increased when the concentration of the vic-dioxime was increased. This fact further substantiates the findings described in Section V.

VII. DISCUSSION

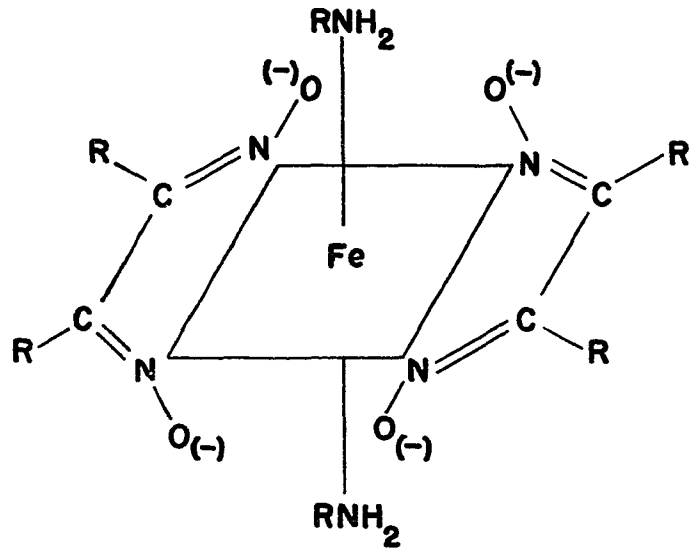
A considerable number of seemingly disconnected facts must be accounted for in any hypothesis attempting to explain the nature of the Fe(II)-vic-dioxime-amine complexes. Banks and Byrd (2) reported the formulation of $Fe(HD)_2 \cdot 2H_2O$ in an acetate buffered solution. The red or violet color of the ternary complexes developed only as the pH of the solution was raised above 7. When an Fe(II) solution was added to a solution containing all the necessary reagents for forming the ternary complex, a number of phenomena were observed. The first color developed gradually changed to another color. The vic-dioxime to iron ratio of the first complex formed was found to be two to one. After the system reached equilibrium a one to one ratio was found. Evidence for the formation of still another complex, presumably two to one, was found when the vic-dioxime was present in great excess. It was shown that at least one complex was an anion by ion migration experiments. Given below is a suggested hypothesis which appears to explain all of these facts.

It was first assumed that the two vic-dioxime molecules involved in the complex of Banks and Byrd (2) form a planar molecule analogous to that found for nickel dimethylglyoxime by Godycki, Rundle, Voter, and Banks (14). This seems to be a reasonable assumption since the planar form is symmetrical and the hydrogen bonds formed would have the effect of in-

creasing the stability. Above and below the plane of the vic-dioxime molecules, two molecules of water are co-ordinated by the iron to give the well known octahedral structure. It is postulated that this complex is also instantaneously formed at a pH of 9.5. Immediately after the formation of this first complex two amine molecules displace the two water molecules. This does not occur at lower pH's since the amine would be present in the ionic rather than the molecular form. The structure of the complex at this point is



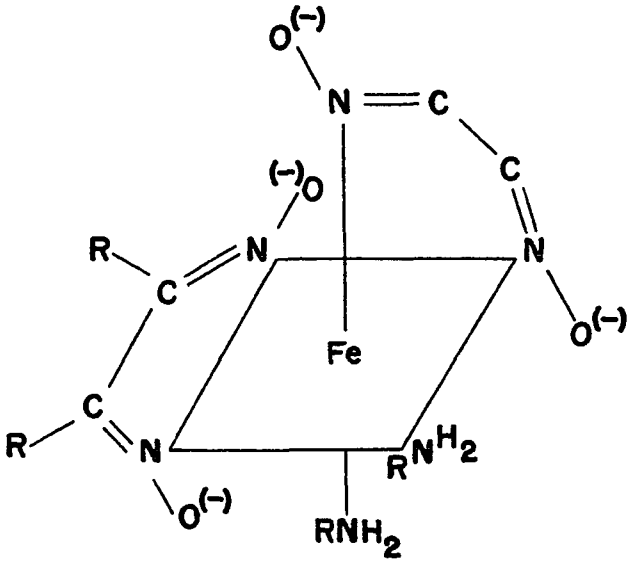
It is this complex which is believed to have given the two to one ratio ten minutes after the initial mixing of the reactants. It is proposed that the bridge hydrogens are then slowly ionized owing to the basic conditions prevalent. The complex would then assume the structure:



In this structure the negative oxygen atoms are in close proximity and there is no longer a hydrogen ion to stand between them as a buffer. This situation could very well cause one of the vic-dioxime molecules to be forced out of the molecule. The action of a vic-dioxime as a dibasic acid has been demonstrated by Feigl and Suter (11). It is also known that nickel dimethylglyoxime is unstable in basic solution and might very well be decomposed by a similar mechanism.

The presence of a neutral, one to one complex has been explained. In order to explain the ion migration results and the spectral changes with high vic-dioxime concentration it is necessary to go further. It is therefore postulated that when the vic-dioxime concentration is sufficiently high, a second molecule returns to the complex but lies in a plane

which is perpendicular to the first vic-dioxime molecule. The structure might be represented by:



In this form the oxygen atoms would be at a greater distance from each other than in the planar two to one complex.

The greater ease of formation of the unsymmetrical two to one complex in the case of the Fe(II)-nioxime-ammonia complex and the Fe(II)-vic-dioxime-ethylenediamine complexes might be explained on the basis of the steric aspects of the situation. Ammonia is the smallest possible amine. Formation of the unsymmetrical two to one complex with the other amines is undoubtedly hindered by the organic radical attached to the nitrogen. In addition, it is known that nioxime forms a stronger complex with Fe(II) than dimethylglyoxime and heptoxime since the iron interference in the nickel determination cannot be prevented with citrate or tartrate. The ethylenediamine cases are explained by the

probability of the ethylenediamine acting as a bidentate ligand and hence reducing the steric hindrance.

For clarity a summary of the proposed mechanism will be given. Upon addition of Fe(II) to the buffered system two vic-dioxime molecules form a planar complex with the iron. Two amine molecules are then substituted into the complex and a slow ionization of the two remaining acidic hydrogen ions on the vic-dioxime molecules follows. When the hydrogen ions are removed, one of the vic-dioxime molecules is forced out due to the repulsion of the negatively charged oxygen atoms. If the vic-dioxime concentration is high enough a second molecule will return to the complex but in a plane perpendicular to the first.

The postulate of Feigl and Suter (11) that the red-violet complex is due to the formation of a salt with the formula $(NH_4)_2\ Fe(D)_2$ does not seem reasonable. If this compound were formed, there seems to be no reason not to expect an identical compound to be formed with potassium. Potassium and ammonium ions are almost identical in their salt forming properties. Potassium does not form such a compound. The only point where ammonium and potassium ions diverge in their properties is in basic solution where ammonia molecules are able to form co-ordination complexes by virtue of their unused pair of electrons.

The study of 2,2'-pyridildioxime has shown that the oxime groups are not in the familiar anti- configuration. This is borne out by the lack of a reaction with Ni(II) and the divergence from the usual acidic ionization constants founds for other vic-dioximes known to have the anti- configuration. The compound was found to be a selective colorimetric reagent for iron, but to have very undesirable kinetic properties. In addition the presence of several different iron complexes renders its use as a colorimetric reagent highly questionable.

The utilization of any of the Fe(II)-vic-dioxime-amine complexes in a colorimetric method for iron is, in the opinion of the author, also very questionable. The fact that a buffer, reducing agent, and amine must be present leads to an overly complicated system. The fact that the determination must be performed at a pH greater than 9.5 means that although the reaction is fairly selective, almost any other metal ion present will be precipitated as the hydroxide or basic carbonate. The fact that the color requires from one half to four hours to stabilize is a definite disadvantage. In addition the presence of an unknown proportion of two different complexes is contrary to the principles of selection of good colorimetric methods. There are already a great number of other colorimetric methods for iron (30, 43), many of which are also mediocre. No further mediocre methods are needed.

In the light of these facts it is believed that no further use should be made of the iron-vic-dioxime-amine reaction as a colorimetric method for iron.

VIII. SUMMARY

The previous work on the Fe(II)-vic-dioxime-amine complexes has been reviewed, analysed, and coupled with additional work. A suggested hypothesis for the mechanism of the reaction has been presented.

The properties of 2,2'-pyridildioxime have been studied generally and especially with regard to its use in the Fe(II)-vic-dioxime-amine reaction. A method for the synthesis and purification of large quantities of 2,2'-pyridildioxime has been presented.

The use of the Fe(II)-vic-dioxime-amine reaction as a colorimetric method has been studied and the method rejected.

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